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(54) Title: HIGH OCTANE UNLEADED AVIATION GASOLINES

(57) Abstract

Novel aviation fuel compositions contain a substantially positive or synergistic combination of an alkyl tertiary butyl ether, an aromatic amine and, optionally, a manganese component. The basefuel containing the additive combination may be a wide boiling range alkylate basefuel.

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HIGH OCTANE UNLEADED AVIATION GASOLINES

BACKGROUND OF THE INVENTION

The invention relates generally to aviation gasoline (Avgas) compositions and methods of making and using such compositions. More particularly, the present invention concerns high octane Avgas compositions containing a non-leaded additive package and methods of making and using such compositions.

Conventional aviation gasoline (Avgas) generally contains an aviation alkylate basefuel and a lead-based additive package. The industry standard Avgas known as 100 Low Lead (100LL) contains the lead additive tetraethyllead (TEL) for boosting the anti-knock property of the Avgas over the inherent anti-knock property of its aviation alkylate basefuel. Knocking is a condition of piston-driven aviation engines due to autoignition, the spontaneous ignition of endgases (gases trapped between the cylinder wall and the approaching flame front) in an engine cylinder after the sparkplug fires. A standard test that has been applied to measure the anti-knock property of lead-based Avgas under various conditions is the motor octane number (MON) rating test (ASTM D2700). Another standard test applied to lead-based Avgas is the supercharge (performance number) rating test (ASTM D909).

Despite the ability of lead-based Avgas to provide good anti-knock property under the severe demands of piston-driven aviation engines, such lead-based compositions are meeting stricter regulations due to their lead and lead oxide emissions. Current U.S. regulations set a maximum amount of TEL for aviation fuels at 4.0 ml/gal and concerns for the negative environmental and health impact of lead and lead oxide emissions may effect further restrictions.

Gaughan (PCT/US94/04985, U.S. Patent No. 5,470,358) refers to a no-lead Avgas containing an aviation basefuel and an aromatic amine additive. The Avgas compositions exemplified in Gaughan reportedly contain an aviation basefuel (e.g., isopentane, alkylate and toluene) having a MON of 92.6 and an alkyl- or halogen-substituted phenylamine that boosts the MON to at least about 98. Gaughan also refers to other non-lead octane boosters such as benzene, toluene, xylene, methyl tertiary butyl ether, ethanol, ethyl tertiary butyl ether, methylcyclopentadienyl manganese tricarbonyl and iron pentacarbonyl, but discourages their use in combination with an aromatic amine because, according to Gaughan, such additives are not capable by themselves of boosting the MON to the 98 level. Gaughan concludes that there is little economic incentive to combine aromatic amines with such other additives because they would have only a very slight incremental effect at the 98 MON level.

It would be desirable to find alternative Avgas compositions that avoid the use of lead-based additives and have good performance in piston-driven aviation engines. It would also be desirable to find Avgas compositions that could use less expensive basefuels.

SUMMARY OF THE INVENTION

The Avgas compositions of the invention contain a combination of non-lead additives (also referred to as the "additive package") including an alkyl tertiary butyl ether and an aromatic amine. The additive package may further include manganese, for example, as provided by methyl cyclopentadienyl manganese tricarbonyl (MMT). In a preferred embodiment, the substantially positive or synergistic additive package is combined with a wide boiling range alkylate basefuel. In a further preferred embodiment, the inventive Avgas composition is an unleaded Avgas having good performance in a piston-driven aviation engine as determined by

one or more ratings including MON, Supercharge and Knock Cycles/Intensity at maximum potential knock conditions of an aviation engine.

The invention is also directed to a method of making an unleaded Avgas composition wherein the additive package is combined with a basefuel, such as a wide boiling range alkylate. The concentration of the additives in the Avgas may be based on a non-linear model, wherein the combination of additives has a substantially positive or synergistic effect on the performance of the unleaded Avgas composition. The invention is further directed to a method of improving aviation engine performance by operating a piston-driven aviation engine with such Avgas compositions.

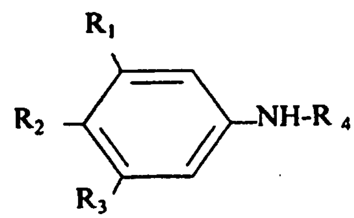
DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

For purposes of the invention, "Avgas" or "Avgas composition" refers to an aviation gasoline. In general, an Avgas is made of a basefuel and one or more additives.

The compositions according to the invention contain a combination of additives including an alkyl tertiary butyl ether and an aromatic amine. The combination may further include a manganese component that is compatible with the other additives and the base fuel, for example, as provided by the addition of methyl cyclopentadienyl manganese tricarbonyl (MMT). The combination of additives is also referred to as "the additive package."

The alkyl tertiary butyl ether in the additive package is preferably a C_1 to C_5 tertiary butyl ether and more preferably methyl tertiary butyl ether (MTBE) or ethyl tertiary butyl ether (ETBE). This component of the additive package is also broadly referred to as the oxygenate.

The aromatic amine in the additive package is preferably of the formula:



where R_1, R_2, R_3 and R_4 are individually hydrogen or a C_1-C_5 alkyl group. In a preferred embodiment, the aromatic amine additive is aniline, n-methyl aniline, n-ethyl aniline, m-toluidine, p-toluidine, 3,5-dimethyl aniline, 4-ethyl aniline or 4-n-butyl aniline.

Methyl cyclopentadienyl manganese tricarbonyl (MMT) may also be included in the additive package, particularly to provide a magnesium component to the additive package.

The inventive Avgas compositions preferably comprise 0.1 to 40 vol% alkyl tertiary butyl ether, 0.1 to 10 wt% aromatic amine and 0 to 0.5 g manganese. For example, the inventive composition may comprise 15 to 32 vol% methyl tertiary butyl ether, 1.5 to 6 wt% aniline and 0 to 0.1 g manganese.

In a preferred embodiment, the additive package has a substantially positive or synergistic effect in the Avgas composition to which it is added. For purposes of this specification, the term "substantially positive," in the context of the additive package, means that a successive additive that is added to the Avgas composition substantially boosts the performance of the Avgas composition. In the case of MON, "substantially positive" effect means that each successive additive boosts the Avgas MON, preferably by 0.5, more preferably by 1.0 and most preferably by 1.5. For example, an Avgas containing a wide boiling range alkylate having a MON of 91.5 and an additive of 10 wt% aniline has a MON of 97.6. When

that Avgas further contains a 40 vol% ETBE, the Avgas MON is boosted to 101.1. Such a composition contains a substantially positive combination of additives because the overall MON of 101.1 is greater than the individual MON levels of 97.6 (10 wt% aniline) and 96.2 (40 vol% ETBE) and the addition of 40 vol% ETBE boosted the MON of the basefuel/10 wt% aniline composition by 3.5.

For purposes of this specification, the term "synergistic," in the context of the additive package, means that the effect of the combined additives is greater than the sum of the performance achieved by the individual additives under the same conditions. In the case of MON, synergistic means that the increase in MON due to the additive package is greater than the sum of MON increases for each additive when it is the sole additive in the basefuel.

These definitions of "substantially positive" and "synergistic" effect are further understood in view of the numerous combinations of additives that result only in antagonistic combinations, wherein the overall MON does not increased or decreases with the addition of other additives.

Combining multiple additives into a package that includes an aromatic amine has been viewed as an undesirable approach to improve the anti-knock property of an Avgas. (See Background of the Invention, Gaughan.) As further shown in the following Table 1, random mixtures of multiple octane boosting additives can result in antagonistic octane effects.

Table 1. Non-linear Blending Octane Effects (Basefuel is wide boiling range alkylate.)

Blend #	ETBE (vol.%)	Mn (g/gal)	Aniline (wt. %)	MON
1	0	0	10	97.6
2	40	0	0	96.2
3	40	0	10	101.1
4	40	0.5	10	97.9

Legend: ETBE = Ethyl Tertiary Butyl Ether, Mn = Manganese Concentration*, MON = Motor Octane
*as provided by a corresponding amount of MMT

As seen in Blend #4, the combination of basefuel/10% wt aniline/40 vol% ETBE/0.5 g/gal manganese results in an antagonistic effect wherein the additive package (40 vol% ETBE/0.5 g/gal Mn/10 wt% aniline) does not boost the MON beyond that of the basefuel to any significant extent. Indeed, this additive package reduces the MON boosting effect of the basefuel/10% wt aniline/40% vol ETBE composition.

In a preferred embodiment, the additive package is combined with a basefuel containing a wide boiling range alkylate. Under this embodiment of the invention, an Avgas can be made with a basefuel not conventionally used for Avgas. Under aviation standards (ASTM D-910), the basefuel in an Avgas is an aviation alkylate, which is a specially fractionated hydrocarbon mixture having a relatively narrow range of boiling points. The inventive additive package may be added to any suitable basefuel wherein the resulting combination of additive package and basefuel is suitable for use as an Avgas, as based on performance characteristics and ratings and not necessarily on ASTM standards. Such basefuels include conventional aviation alkylates (e.g. within the specifications of ASTM-910, including specifications for boiling points and distillation temperatures) and wide boiling range basefuels.

For purposes of this specification, the term "wide boiling range alkylate" is defined as an alkylate containing components having a range of boiling points that is substantially wider than the range of boiling points in an aviation alkylate basefuel. Preferably, the wide boiling range alkylate contains hydrocarbons having a range of boiling points up to at least about 350°F. More preferably, the boiling range is from about 85°F ± 10°F to about 400°F ± 15°F (which essentially corresponds to an automotive gasoline basefuel). The following Table 2 provides an example of an aviation alkylate and a wide boiling range alkylate.

Table 2: Comparison of Wide boiling Range Alkylate and Aviation Alkylate Fuels.					
Tests	Wide boiling range alkylate	Aviation Alkylate	Tests	Wide boiling range alkylate	Aviation Alkylate
	Distillation Results		API	71.5	73.0
IBP*	88.1 °F	97.7 °F			
10 %	147.9	155.3	RVP	7.6 psi	6.5 psi
20 %	179.4	178.5			
30 %	199.2	195.8	Paraffins	99.2 vol.%	99.4 vol.%
40 %	209.8	206.0	Olefins	0.2 vol.%	0.4 vol.%
50 %	216.6	212.1	Aromatics	0.6 vol.%	0.2 vol.%
60 %	222.4	215.7			
70 %	228.7	218.6	MON	91.4	93.9
80 %	238.6	221.3	RON	93.4	97.1
90 %	262.9	224.9			
FBP*	397.2	233.4	Perf.No.	85.4	97.4
Legend: IBP = Initial Boiling Point, EBP = Final Boiling Point, API = API Gravity, RVP = Reid Vapor Pressure @ 100F, RON = Research Octane Number, MON = Motor Octane Number, Perf.No. = Performance Number (ASTM - D909)					

The lower octane of the wide boiling range alkylate compared to the aviation alkylate is due primarily to lower amounts of inherently high octane hydrocarbons, isopentane and isooctane, as well as higher amounts of higher molecular weight, higher boiling paraffins. Table 3 presents gas chromatographic analyses of the aviation industry standard 100 Low Lead, which uses aviation alkylate as the primary base stock (e.g., at least 88% vol) and the wide boiling range alkylate and demonstrates the lower concentrations of isopentane and the isooctane isomers in the wide boiling range alkylate.

Table 3. Comparison of Wide Boiling Range Alkylate and 100 Low Lead

	Concentration in 100 Low Lead (wt%)	Concentration in Wide Boiling Range Alkylate (wt%)
Isopentane	9.26	5.04
2,2,4-trimethylpentane	30.93	21.89
2,2,3-trimethylpentane	1.06	1.40
2,3,4-trimethylpentane	9.91	10.99

The distillation curve temperatures for the second half of the wide boiling range alkylate are considerably higher than the aviation alkylate because of the higher molecular weight paraffinic hydrocarbons present in the former.

A common result of having a higher concentration of larger paraffins, particularly with the straight chain or normal paraffins, is a lower octane value. The larger paraffin molecules present in the wide boiling range alkylate typically undergo more and faster isomerization chemical reaction steps during the low temperature portion of the oxidation chemistry leading to auto-ignition. Isomerization steps in paraffin chemistry are very fast routes to free radical propagation and subsequent autoignition. The oxidation steps leading to autoignition between the two alkylate basefuels are different thus requiring different fuel and additive formulations for optimal performance. Substituting high octane oxygenates for a substantial proportion of the alkylate basefuel reduces the number of rapid isomerization reactions and replaces them with less reactive partial oxidation intermediates, thereby increasing the octane value of the fuel.

The preferred embodiment of the invention that uses the wide boiling range alkylate as a basefuel offers a high quality, high performance alternative to conventional Avgas. Such wide boiling range alkylate basefuels offer a greater choice of basestocks for Avgas formulations and also likely provide a less expensive basefuel for Avgas compared to the conventional aviation alkylate basefuel.

In a preferred embodiment, the compositions according to the invention have good performance in piston-driven aviation engines. Preferably that performance is determined by one or more ratings including MON, Supercharge and Knock Cycles/Intensity at maximum potential knocking conditions in an aircraft engine. The inventive Avgas compositions preferably have a

MON of at least about 94, more preferably at least about 96 and most preferably at least about 98. Further preferred Avgas compositions have a MON of at least about 99 or more preferably at least about 100. For example, a preferred MON range may be from about 96 to about 102. The Supercharge rating is preferably at least about 130. The inventive Avgas compositions also preferably minimize, or eliminate, knocking in a piston-driven aircraft engine at maximum potential knocking conditions. The Knock Cycle rating is preferably less than (average) 50 per 400 cycles and the Knock Intensity rating is preferably less than 30 per cycle.

The invention is also directed to a method for preparing an Avgas composition that involves combining a basefuel, such as a wide boiling range alkylate, with an additive package. The content and concentration of the additive package is preferably selected from an inventive non-linear model that identifies substantially positive or synergistic additive packages. The method preferably identifies Avgas compositions that have good performance in piston-driven aviation engines based on ratings of MON, Supercharge and/or Knock Cycles/Intensity.

The invention is further directed to a method for operating a piston-driven aircraft that involves operating the piston-driven engine with an Avgas composition made by a composition according to the invention.

EXAMPLES

A. Determination of MON

The MON rating test (ASTM D2700) is conducted using a single cylinder variable-compression laboratory engine which has been calibrated with reference fuels of defined octane levels. The sample of interest is compared to two reference fuels at standard knock intensity and the octane number of the sample is determined by bracketing or compression ratio (c.r.) methods.

In bracketing, the octane value of the sample is determined by interpolating between two reference fuel octane values. In the c.r. method, the octane value of the sample is determined by finding the compression ratio which duplicates the standard knock intensity of a reference fuel and the octane number is then found in a table of values. Repeatability limits for MON determination at 95% confidence intervals is 0.3 MON for 85-90 MON fuels while reproducibility limits are 0.9 for 85 MON and 1.1 for 90 MON.

B. Determination of Supercharge Rating

The Supercharge rating test (ASTM - D909) determines the knock-limited power, under supercharge rich-mixture conditions, of fuels for use in spark ignition reciprocating aircraft engines. The Supercharge rating is an industry standard for testing the severe octane requirements of piston driven aircraft. For purposes of this application, "ASTM-D909" is used interchangeably with both "supercharge rating" and "performance number."

C. Determination of Knock Cycles and Intensity Rating

For purposes of this application, "Knock Cycle/Intensity rating test" and "Lycoming IO-360 tests" are used interchangeably. The Knock Cycles/Intensity rating test was performed with a Textron Lycoming IO-360 engine ("the Lycoming engine") on a dynamometer test stand (See FIG. 1). Each of the four cylinders of the Lycoming engine was equipped with a Kistler 6061B piezoelectric transducer. These transducers produce electric charges proportional to the detected pressures in the combustion chambers in the Lycoming Engine. The charge was then passed into four Kistler 5010 charge mode amplifiers which were calibrated so that output voltage from the amplifiers was equivalent to 20 atmospheres as read by the detector. The voltage was processed

through a National Instruments NB-A2000 A/D board which reads all four channels simultaneously at a rate of 250,000 samples per second at a resolution of 12 bits.

The data acquisition was facilitated by a computer program (See FIG. 2) using National Instruments' Labview programming environment. The data acquisition program stores the data from 200 to 400 consecutive firings from the engine which is typically operated at 2700 rpm, wide open throttle at an equivalence ratio of about 1.12 and maximum cylinder temperature of just below 500°F. The data is first stored into buffers, then into the Random Access Memory of a MacIntosh 8100/80 Power PC and finally on the hard drive. The raw data files were then backed up onto magneto-optical discs and post-processed using a Labview program.

Before storage and processing, data from the individual combustion chamber firings were passed through a Butterworth 4th order digital bandpass filter of 15kHz-45kHz range. This is done to isolate frequencies which could only be significantly excited within the combustion chamber by a knocking event. The filtered signal was then "windowed" for 3 milliseconds near top dead center of piston travel (compression/expansion stroke). The filtered, windowed signal was then sent through an absolute-value function and integrated to obtain a pressure-time-intensity expression of the acoustic energy supplied to the filter in the 15kHz-45kHz band of frequencies detected by the system. This value was used to create a scale with which knock intensity was measured. If the intensity of the integral was found to be greater than 20 on this scale, it was determined to be a knocking case and the knocking events per 200 cycles were recorded.

D. Determination of Non-Linear Models for Identifying Aviation Fuel Compositions with Desirable MON Ratings

The effects of various fuel formulations on MON ratings were determined using statistically designed experiments. More specifically, the complex relationships between the in-cylinder oxidation chemistries of the octane boosting additives and the basefuel were investigated using face centered cube statistical designs (See, e.g., Fig. 3).

The statistically designed experiments measured the MON values of specific fuel formulations which were combinations of three variables (Manganese level, aromatic amine level and oxygenate level) mixed with a wide boiling range alkylate. The three variables and their respective concentration ranges define the x, y and z axes of the cube. (See Fig. 3). The cube faces (surfaces) and the space within the cube define all the interaction points for investigation. The three variable test ranges were 0-10 wt% aromatic amine, 0-0.5 g/gal manganese (Mn) and 0-40 vol. % oxygenate (an alkyl tertiary butyl ether). The manganese may be provided by a corresponding amount of methyl cyclopentadienyl manganese tricarbonyl (MMT). The two oxygenates tested were methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE). In total, four test cubes were designed to measure the numerous fuel combinations and therefore potentially different chemical oxidation interactions. The four cube design layouts are listed in Table 4. Aniline and n-methyl aniline were the aromatic amines chosen for complete statistical analyses.

Table 4. Design for Testing Cube Independent Variables.

Cube Number	Basefuel	Variable 1	Variable 2	Variable 3
1	Wide boiling range	MMT	MTBE	Aniline
2	Wide boiling range	MMT	ETBE	Aniline
3	Wide boiling range	MMT	MTBE	n-Methyl Aniline

Table 4. Design for Testing Cube Independent Variables.				
Cube Number	**Basefuel**	**Variable 1**	**Variable 2**	**Variable 3**
4	Wide boiling range	MMT	ETBE	n-Methyl Aniline

The MON values were measured at specific points along the three cube axes as well as the cube center point. Multiple measurements were made at the center point to calculate the MON variation level with the assumption being it is constant over all the test space of the design, i.e. essentially a ten MON number range, 91-101. Polynomial curves were fitted to the data to define equations which describe the three variable interactions with respect to MON over the entire cube test space. From these equations, the MON performance for all variable combinations can be predicted within the test space defined by the maximum and minimum concentration ranges of the variables. Some of the predicted and measured MON values have been summarized in Tables 5-8. The remainder of the predicted values can be derived from the prediction equations.

Table 5. Predicted MON versus Measured MON for Oxygenate + Aniline
Manganese = 0 g/gal

Aniline	0 wt%		2wt%		6wt%		10wt%	
Vol.% MTBE	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)
0	91.5	91.1	93.8	94.6	97.1		98.6	98.8
10	92.8		95.0		98.0		99.3	
20	93.8	93.6	95.8		98.6	98.9	99.6	
30	94.4		96.3		98.8		99.6	
40	94.7	95.2	96.5	97.0	98.7		99.2	99.0
Aniline	**0 wt%**		**2wt%**		**6wt%**		**10wt%**	
Vol.% ETBE	**MON (p)**	**MON (m)**	**MON (p)**	**MON (m)**	**MON (p)**	**MON (m)**	**MON (p)**	**MON (m)**
0	92.3	91.1	93.8	95.9	96.8		99.7	97.6
10	94.6		95.9		98.5		101.1	
20	96.0	94.0	97.2		99.4	98.8	101.7	
30	96.6		97.5		99.4		101.3	
40	96.3	96.2	97.0	97.2	98.6		100.1	101.1

Table 6. Predicted MON versus Measured MON for Oxygenate + Aniline Manganese = 0.5 g/gal								
Aniline	0 wt%		2wt%		6wt%		10wt%	
Vol.% MTBE	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)
0	96.0	95.3	97.4	97.7	98.9		98.7	99.1
10	97.3		98.5		99.8		99.4	
20	98.2	99.1	99.4		100.4	99.6	99.7	
30	98.9		99.9		100.6		99.7	
40	99.2	100.3	100.1	99.6	100.6		99.3	99.8
Aniline	0 wt%		2wt%		6wt%		10wt%	
Vol. ETBE	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)
0	95.5	95.5	95.9	96.0	96.8		97.6	97.8
10	97.8		98.0		98.5		99.0	
20	99.2	97.5	99.3		99.4	100.5	99.5	
30	99.8		99.6		99.4		99.2	
40	99.4	98.4	99.1	100.9	98.6		98.0	97.1

Table 7. Predicted MON versus measured MON for Oxygenate + n-Methyl Aniline Manganese = 0.0 g/gal								
n-Methyl Aniline	0wt%		2wt%		6wt%		10wt%	
Vol. MTBE	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)
0	92.1	91.1	93.4	94.0	95.0		95.4	94.7
10	92.6		93.7		95.0		95.0	
20	93.2	93.6	94.1		95.0	94.9	94.6	
30	93.7		94.5		95.0		94.2	
40	94.3	95.2	94.8	94.8	95.0		93.9	94.6
n-Methyl Aniline	0wt%		2wt%		6wt%		10wt%	
Vol.% ETBE	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)
0	92.1	91.1	92.8	93.8	94.1		95.4	95.6
10	93.3		93.8		94.6		95.5	
20	94.5	94.0	94.7		95.2	95.9	95.6	
30	95.7		95.7		95.7		95.7	
40	96.9	96.2	96.6	96.2	96.2		95.8	96.5

Table 8. Predicted MON versus measured MON for Oxygenate + n- Methyl Aniline, Manganese = 0.5 g/gal

n-Methyl Aniline	0wt%		2wt%		6wt%		10wt%	
Vol.% MTBE	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)
0	97.2		97.7	99.4	97.7		96.4	95.9
10	97.7		98.0		97.7		96.0	
20	98.3		98.4		97.7	97.5	95.6	
30	98.8		98.8		97.7		95.3	
40	99.4		99.1	98.7	97.7		94.9	95.3

n-Methyl Aniline	0wt%		2wt%		6wt%		10wt%	
Vol.% ETBE	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)	MON (p)	MON (m)
0	96.6		96.3	97.4	95.9		95.5	95.9
10	97.1		96.9		96.4		96.0	
20	97.6		97.4		96.9	97.2	96.5	
30	98.2		97.9		97.5		97.0	
40	98.7		98.5	97.3	98.0		97.5	98.4

The equations which describe the three variable (oxygenate, Manganese and aromatic amine) interactions and ultimately predict MON levels are listed in Table 8A.

Table 8A. MON Prediction Equations

Test Cube: MTBE/Aniline/Manganese

MON = 91.54 + (0.1466 x MTBE) + (8.827 x Mn) + (1.252 x Aniline) - (0.006492 x MTBE x Aniline) - (0.8673 x Mn x Aniline) - (0.001667 x MTBE^2) - (0.05437 x Aniline^2)

Test Cube: MTBE/n-Methyl Aniline/Manganese

MON = 92.06 + (0.05563 x MTBE) + (10.23 x Mn) + (0.7308 x nMA) - (0.009273 x MTBE x nMA) - (0.8220 x Mn x nMA) - (0.04005 x nMA^2)

Test Cube: ETBE/Aniline/Manganese

MON = 92.32 + (0.2730 x ETBE) + (6.349 x Mn) + (0.7429 x Aniline) - (0.009016 x ETBE x Aniline) - (1.058 x Mn x Aniline) - (0.004362 x ETBE^2)

Test Cube: ETBE/n-Methyl Aniline/Manganese

MON = 92.12 + (0.1185 x ETBE) + (17.04 x Mn) + (0.3317 x nMA) - (0.1306 x ETBE x Mn) - (0.01099 x ETBE x nMA) - (0.8828 x Mn x nMA) + (0.0218 x ETBE x Mn x nMA) - (16.36 x Mn^2)

The predicted MON variability for all four design cubes is a combination of engine measurement, fuel blending and equation fitting variability. Table 9 shows the MON engine measurement variability in terms of standard deviations for the four test cubes.

Table 9. Standard Deviations for Four Test Cubes.

MTBE, Aniline, Mn	0.70 MON	ETBE, Aniline, Mn	0.28 MON
MTBE,n-Methyl Aniline,Mn	0.60 MON	ETBE, n-Methyl Aniline, Mn	0.55 MON

The pooled standard deviations for the four test cubes is 0.614 with 18 degrees of freedom. At the 95% confidence limit this results in a variability of 1.83 MON. Variability, as used here, is defined as it is in ASTM MON rating method D-2700--for two single MON measurements, the maximum difference two numbers can have and still be considered equal. However, variability as used here is neither purely repeatability nor reproducibility, but is somewhere between the two definitions. All 168 test fuels were blended from the same chemical/refinery stocks and randomly MON rated by two operators on two MON rating engines over an 8 week period. The accuracy and variability for the equation fitting process of the MON data is shown in Table 10.

Table 10. Equation Fitting Variability

Test Cube	R^2 Value	Root Mean Squared Error	Average Error
MTBE + Aniline	91.0	0.82	0.54
ETBE + Aniline	74.5	1.29	0.88
MTBE + n-Methyl Aniline	77.3	0.99	0.70
ETBE + n-Methyl Aniline	81.3	0.81	0.61

The R^2 Values are the proportion of variability in the MON that is explained by the model over the ten octane number range tested. The fuel blending variability was not quantified but is not expected to be a major contributor to the overall predicted MON variability.

The majority of MON results were obtained while the aromatic amines were set in the statistical cube design as aniline and n-methyl aniline. Subsequent work was done to determine other potentially high octane aromatic amines. (See Tables 11-13.) Specific aromatic amines were substituted into two different blends; 1) 80 vol.% wide boiling range alkylate + 20 vol.% MTBE and 2) 80 vol.% wide boiling range alkylate + 20 vol.% ETBE. The substituted aromatic amines were blended at 2.0 wt%. No manganese was added to these blends. The MON results listed in Tables 11-13 are average MON of two tests.

Table 11: MON Values for Methyl Substitutions on Aniline Ring

	80/20 vol% Wide boiling range alkylate + MTBE		80/20 vol% Wide boiling range alkylate + ETBE	
aromatic amine	MON	dMON*	MON	dMON*
Aniline	96.3	---	97.3	---
o-toluidine	94.5	-1.8	95.2	-2.1
m-toluidine	96.8	0.5	97.4	0.1
p-toluidine	96.8	0.5	96.8	-0.5

* Note: dMON = delta MON = difference between additive of interest and Aniline reference point.

Table 12. MON Values for di- and tri- methyl substitutions on Aniline Ring

	80/20 vol% Wide boiling range alkylate + MTBE		80/20 vol% Wide boiling range alkylate + ETBE	
aromatic amine	MON	dMON*	MON	dMON*
Aniline	96.3	---	97.3	---
2,3-dimethyl Aniline	93.8	-2.6	94.2	-3.1
2,4-dimethyl Aniline	95.0	-1.3	95.2	-2.1
2,5-dimethyl Aniline	93.9	-2.4	95.3	-2.1
2,6-dimethyl Aniline	93.3	-3.0	93.4	-3.9
3,5-dimethyl Aniline	95.7	-0.6	96.7	-0.6
2,4,6-trimethyl Aniline	92.6	-3.8	93.7	-3.6

Table 13. MON Values for Alkyl Substitutions on Aniline's Amine.

	80/20 vol% Wide boiling range alkylate + MTBE		80/20 vol% Wide boiling range alkylate + ETBE	
aromatic amine	MON	dMON*	MON	dMON*
Aniline	96.3	---	97.3	---
4-ethyl Aniline	96.1	-0.3	97.5	0.2
4-n-butyl Aniline	95.7	-0.6	96.9	-0.5
n-methyl Aniline	95.0	-1.3	95.7	-1.6
n-ethyl Aniline	91.9	-4.4	91.9	-5.4

It can be seen from Tables 11-13 that the aromatic amines which have a methyl substitution in the ortho- (or the 2 position) on the aromatic ring as well as the n-alkyl

substitutions on the amine are not effective octane boosting additives for these two basefuels. However, the meta- ring position, (positions 3- and 5-) and the para- ring position, (position 4-) methyl substituted aromatic amines are generally more effective octane boosting additives for this basefuel with the exception of the p-toluidine in the ETBE/basefuel case. The relative MON increasing effectiveness of the different alkyl substituted aromatic amines exemplifies the importance of mapping the chemical oxidation reaction routes for the additives of interest relative to the MON test environment. Further data from these experiments are shown in FIGS. 4-15.

E. Determination of Non-linear Models for Identifying Aviation Fuel Compositions with Desirable MON, Supercharge, and Knock Cycle/Intensity Ratings

To better characterize the performance of fuel formulations, the effects of various fuel formulations on MON, Supercharge and Knock Cycle/Intensity ratings were determined using statistically designed experiments. The subject fuel compositions were combinations of MTBE, aniline and manganese components and the same wide boiling range alkylate fuel as the previous designs. The three variable test ranges for these experiments were 20-30 vol % MTBE, 0-6 wt% aniline and 0 - 0.1 g/gal manganese. Anti-knock ratings of MON, Supercharge and Knock Cycle/Intensity ratings were measured at least in duplicate.

Table 14 shows the non-linear interactions of the fuel composition components on the Supercharge rating and average Knocking Cycles and average Knock Intensity per 400 consecutive engine cycles data. The eight fuel formulations shown represent the extremes of the ranges tested.

Statistical analysis shows an interaction between the MTBE and manganese terms in the equations for supercharge rating but only when aniline levels are low with respect to the domain tested. There is another significant interaction for supercharge rating which is that as MTBE increases the interaction between manganese and aniline becomes antagonistic. Also, the data analysis for Knock Intensity contains an antagonistic interaction between MTBE and aniline. The Knocking Cycles data demonstrates a three way interaction between the MTBE, manganese and aniline.

Table 14: Measured Octane Parameters with respect to Fuel Formulation

MTBE (vol %)	Mn (g/gal)	Aniline (wt %)	MON	Supercharge Rating	Average Knocking Cycles / 400	Average Knock Intensity / 400
20	0.00	0	95.4	115.5	121	49
20	0.00	6	97.6	140.2	12	32
20	0.10	0	95.6	118.1	68	40
20	0.10	6	98.0	142.5	4	24
30	0.00	0	96.2	114.1	66	35
30	0.00	6	98.3	143.9	2	33
30	0.10	0	97.4	133.5	13	33
30	0.10	6	99.3	144.5	2	20

Because of the above mentioned non-linear fuel composition interactions, neither MON nor supercharge ratings when considered individually will always predict the knock-free operation of the commercial Lycoming IO-360 aviation engine. (See Table 15). The Knocking Cycle and Knock Intensity data in Table 15 are the average of duplicate 400 cycle tests.

Table 15: Measured Octane Parameters with respect to Fuel Formulation (II)

Fuel Number	MON	Supercharge Rating	Average Knocking Cycles / 400	Average Knock Intensity / 400
1	98.4	134.9	17	30
2	98.5	142.2	0	0
3	96.5	136.1	0	0
4	96.3	115.1	73	35

The R^2 values between MON, Supercharge, Knocking Cycles and Knock Intensity are listed in Table 16.

Table 16: R^2 values for Knocking Cycles and Knock Intensity Predictions	
Combination	**R^2 values**
MON to predict Knocking Cycles*	**.44**
MON to predict Knock Intensity*	**.38**
Supercharge to predict Knocking	**.64**
Supercharge to predict Knock Intensity*	**.82**
Notes: (*) Outlying data points that were not representative of population were removed after statistical analyses.	

Table 17 includes the references of pure isooctane as well as the industry standard leaded Avgas 100 Low Lead. For example, pure isooctane has a MON value of 100 by definition but knocks severely in the Lycoming IO-360 at its maximum potential knock operating condition. Addition of tetraethyllead (TEL) to isooctane is required to boost the supercharge rating sufficiently high to prevent auto-ignition in a commercial aircraft engine.

Table 17: Knock Data for Isooctane and Leaded Avgas 100 Low Lead

Fuel	MON	Supercharge Rating	Knocking Cycles / 400	Knock Intensity / 400
Isooctane	100	100	85	Not Collected
100 Low Lead	105	131.2	0	0

Using centered & scaled units for the fuel properties our equation for MON is:

$$MON = 97.75 + 0.575*MTBE(s) + 0.305*Mn(s) + 1.135*Aniline(s) - 0.485*Mn(s)^2.$$

Converting to actual units yields:

$$MON = 92.95 + 0.115*MTBE + 25.5*Mn + 0.3783*Aniline - 194*Mn^2.$$

No interactions were statistically significant.

Using centered & scaled units for the fuel properties our equation for supercharge (SC) is:

$$SC = 140.008 + 2.325*MTBE(s) + 3.9*Mn(s) + 11.715*Aniline(s)$$
$$+ 1.89375*MTBE(s)*Mn(s) - 2.39375*Mn(s)*Aniline(s)$$
$$- 2.30625*MTBE(s)*Mn(s)*Aniline(s)$$
$$- 8.653*Aniline(s)^2.$$

Converting to actual units yields:

$$SC = 122.72 - 0.375*MTBE - 294.125*Mn + 6.628*Aniline$$
$$+ 16.8*MTBE*Mn + 0.15375*MTBE*Aniline + 60.917*Mn*Aniline$$
$$- 3.075*MTBE*Mn*Aniline$$
$$- 0.9614815*Aniline^2$$

Looking at the equation in centered and scaled units, we see that the interaction between MTBE and Mn is synergistic (coefficient same sign as coefficients for individual effects of MTBE * Mn). But, because of the presence of the 3-way interaction between MTBE, Mn, and Aniline, the size of the MTBE*Mn interaction actually depends on the level of aniline. At the low level of aniline, the MTBE*Mn interaction is synergistic, but as the aniline level increases, the MTBE*Mn interaction becomes less and less synergistic until it becomes basically zero at the high aniline level (if anything, it is antagonistic at this point). Thus, there is a synergism between MTBE and Mn, but generally only at low levels of aniline.

A similar description can be used for the Mn*Aniline interaction, where the size of this interaction depends on the MTBE level. At low levels of MTBE, the Mn*Aniline interaction is essentially zero, but as the MTBE level increases the Mn*Aniline interaction becomes more and more antagonistic. Table 18 below illustrates the above concepts.

Table 18

MTBE (vol %)	Mn (g/gal)	Aniline (wt %)	Actual SC	Predicted SC	Expected SC[1]
20	0.00	0	122.2, 108.7	115.2	
20	0.10	0	116.8, 119.4	119.4	
30	0.00	0	113.0, 115.1	111.5	
30	0.10	0	132.1, 134.9	132.5	115.7
20	0.00	6	137.6, 142.8	138.8	
20	0.10	6	142.7, 142.8	142.7	
30	0.00	6	143.8, 143.9	144.3	
30	0.10	6	143.9, 145.1	146.5	148.2

1 - This is the expected SC value if there was no interaction, that is if the effects of each of the fuel components were additive.

Using centered and scaled units for the fuel properties our equation for Knock Intensity (KInt) is:

$$\text{KInt} = 26.5 - 2.138719*\text{MTBE(s)} - 1.905819*\text{Mn(s)} - 5.877127*\text{Aniline(s)}$$
$$+ 2.477696*\text{MTBE(s)}*\text{Aniline(s)} + 2.711142*\text{Mn(s)}^2 + 2.780729*\text{Aniline(s)}^2$$

Converting to actual units yields:

$$\text{KInt} = 62.9 - 0.923283*\text{MTBE} - 146.56206*\text{Mn} - 7.9423549*\text{Aniline}$$
$$+ 0.1651797*\text{MTBE}*\text{Aniline} + 1084.4568*\text{Mn}^2 + 0.3089699*\text{Aniline}^2$$

Again looking at the equation in the centered and scaled units, we see that the MTBE*Aniline interaction is antagonistic. Also, note that this interaction does not depend on the Mn level because there is no 3-way interaction in the model. The following Table 19 illustrates this interaction.

Table 19

MTBE (vol %)	Mn (g/gal)	Aniline (wt %)	Actual Knock Int.	Predicted Knock Int.	Expected Knock Int.[1]
20	0.00	0	52.0, 48.1, 38.0	44.4	
20	0.00	6	36.1, 27.3, 26.0	27.7	
30	0.00	0	34.4, 35.3	35.2	

MTBE (vol %)	Mn (g/gal)	Aniline (wt %)	Actual Knock Int.	Predicted Knock Int.	Expected Knock Int.[1]
30	0.00	6	25.7, 40.0	28.4	18.5
20	0.10	0	39.4, 40.9, 38.7	40.6	
20	0.10	6	19.0, 28.4, 19.0	23.9	
30	0.10	0	37.6, 30.0, 28.0	31.4	
30	0.10	6	21.0, 19.0	24.6	14.7

1 - This is the expected Knock Intensity value if there was no interaction, that is if the effects of each of the fuel components were additive.

It should be pointed out that knock intensity values below 20 cannot be distinguished from each other, so the antagonistic effect of the MTBE*Aniline interaction may not be quite so significant at the high level of Mn (since the expected value under the assumption of no interaction is 14.7 and the actual values were 21.0 & 19.0).

Using centered and scaled units for the fuel properties, our equation for number of Knocking Cycles (Cycles) is:

$$Y = \ln(\text{Cycles} + 1) = 1.529878 - 0.43339*\text{MTBE(s)} - 0.376319*\text{Mn(s)} - 1.469152*\text{Aniline(s)} + 0.368344*\text{MTBE(s)}*\text{Mn(s)}*\text{Aniline(s)} + 0.732549*\text{Aniline(s)}^2.$$

Converting to actual units yields:

$$Y = \ln(\text{Cycles} + 1) = 4.4331281 - 0.0130092*\text{MTBE} + 29.308018*\text{Mn} - 0.3641767*\text{Aniline} - 1.4733759*\text{MTBE}*\text{Mn} - 0.0245563*\text{MTBE}*\text{Aniline} - 12.278133*\text{Mn}*\text{Aniline} + 0.4911253*\text{MTBE}*\text{Mn}*\text{Aniline} + 0.0813943*\text{Aniline}^2.$$

In either case, the predicted number of knocking cycles is equal to $e^Y - 1$.

This variable was analyzed on the natural log (ln) scale because it was observed that the variability was a function of mean level. Analyzing the data on the ln scale causes the variability to be more constant across mean levels, which is necessary for the statistical tests performed to be valid. Also, since some observations had values of zero for number of knocking cycles (the natural log of zero cannot be calculated), 1 was added to every observation so that the ln transformation could be used. Thus, 1 must be subtracted from Y above to get back to the original units.

Because of the presence of the 3-way interaction in the model and no 2-way interactions, the 3-way interaction can be interpreted in 3 ways. We could say that there is a synergistic interaction between MTBE & Mn at low levels of aniline and an antagonistic interaction at high levels of aniline. This description holds for all pairs of fuel properties.

The following Table 20 describes the MTBE*Mn interaction being synergistic at low levels of aniline and being antagonistic at high levels of aniline

Table 20

MTBE (vol %)	Mn (g/gal)	Aniline (wt %)	Avg. # of Knocking Cycles	Pred. # of Knocking Cycles	Expected # of Knocking Cycles[1]
20	0.00	0	178.5, 93.0, 28.0	63.9	
20	0.10	0	78.5, 48.0, 71.5	62.9	
30	0.00	0	56.5, 73.0	56.0	
30	0.10	0	17.0, 0.8, 17.0	11.9	55.1
20	0.00	6	13.0, 15.5, 0.5	6.2	
20	0.10	6	0.0, 5.5, 0.0	0.6	
30	0.00	6	1.5, 0.5	0.4	
30	0.10	6	1.0, 0.0	0.4	0.0

1 - This is the expected avg. # of knocking cycles value if there was no interaction, that is if the effects of each of the fuel components were additive.

Note that at the high aniline level, the reason for the antagonistic MTBE*Mn interaction is that the number of knocking cycles cannot be reduced to a value lower than zero. Increasing Mn to 0.10 lowers the number of knocking cycles to almost zero and increasing MTBE to 30 also lowers the number of knocking cycles to almost zero. Therefore, increasing both Mn and MTBE at the same time cannot reduce the number of knocking cycles any more.

Using centered and scaled units for the fuel properties our equation for # of Knocking Cycles is:

$$\begin{aligned}\text{Cycles} = {} & 4.462241 - 9.166427*\text{MTBE(s)} - 7.93772*\text{Mn(s)} - 26.077604*\text{Aniline(s)} \\ & + 8.742241*\text{MTBE(s)}*\text{Aniline(s)} + 8.491223*\text{Mn(s)}*\text{Aniline(s)} \\ & + 5.167309*\text{MTBE(s)}*\text{Mn(s)}*\text{Aniline(s)} \\ & + 24.483337*\text{Aniline(s)}^2.\end{aligned}$$

Converting to actual units yields:

$$\begin{aligned}\text{Cycles} = {} & 135.2 - 2.5482718*\text{MTBE} + 188.15204*\text{Mn} - 33.803388*\text{Aniline} \\ & - 20.669236*\text{MTBE}*\text{Mn} + 0.2383288*\text{MTBE}*\text{Aniline} - 115.63548*\text{Mn}*\text{Aniline} \\ & + 6.8897453*\text{MTBE}*\text{Mn}*\text{Aniline} \\ & + 2.7203708*\text{Aniline}^2 .\end{aligned}$$

In this case, the only synergistic interaction is between MTBE and Mn at low aniline levels. All other interactions are antagonistic. The MTBE*Mn synergism at low aniline levels and antagonism at high aniline levels is shown below in Table 21.

Table 21

MTBE (vol %)	Mn (g/gal)	Aniline (wt %)	Avg. # of Knocking Cycles	Pred. # of Knocking Cycles	Expected # of Knocking Cycles[1]
20	0.00	0	178.5[2], 93.0, 28.0[2]	84.2	
20	0.10	0	78.5, 48.0, 71.5	61.7	
30	0.00	0	56.5, 73.0	58.7	
30	0.10	0	17.0, 0.8, 17.0	15.5	36.2
20	0.00	6	13.0, 15.5, 0.5	7.9	
20	0.10	6	0.0, 5.5, 0.0	0.0	
30	0.00	6	1.5, 0.5	0.0	
30	0.10	6	1.0, 0.0	8.2	0.0

1 - This is the expected avg. # of knocking cycles value if there was no interaction, that is if the effects of each of the fuel components were additive.

2 - These observations were not included in the analyses.

Further data from these experiments are shown in FIGS. 16-30.

The testing and equation fitting variability of the second set of experimentally designed cubes is demonstrated in Tables 22 and 23. For the predicted performance parameter listed in Table 22, the 95% total variability is a combination of engine measurement and fuel blending variabilities. Table 22 also shows the performance parameter engine measurement and fuel blending variability in terms of standard deviation and total variability calculated at the 95% confidence limit.

Table 22: Variability Analysis for Second Cube Sets		
Performance Parameter	Standard Deviation	95% Total Variability
MON	0.69	2.07
Performance Number	3.93	11.73
Knock Intensity	7.04	19.70
Knocking Cycles (ln Scale)	1.15	3.27
Knocking cycles (linear Scale)	18.6	52.60

Total variability, as used here, is defined as it is in ASTM Methods -- for two single measurements, the maximum difference two numbers can have and still be considered equal. However, variability as used here is neither purely repeatability nor reproducibility, but is somewhere between the two definitions. The accuracy and variability for the equation fitting process of the performance parameters is shown in Table 23.

Table 23: Equation Fitting Variability for Second Cube Set

Performance Parameter	R^2 Value	Root Mean Squared Error	Average Error
MON	76.8	0.63	0.47
Performance Number	91.2	3.99	2.50
Knock Intensity	60.5	5.40	3.80
Knocking Cycles (in small "L" Scale)	74.2	0.83	0.60
Knocking Cycles (linear Scale)	89.1	9.30	7.10

Other features, advantages and embodiments of the invention disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosure. In this regard, while specific embodiments of the invention have been described in detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.

CLAIMS:

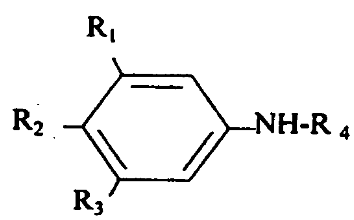
1. An unleaded aviation fuel composition comprising:

(1) an unleaded basefuel and

(2) a substantially positive or synergistic combination of

(a) an alkyl tertiary butyl ether, and

(b) an aromatic amine having the formula



wherein R_1, R_2, R_3 and R_4 are hydrogen or a C_1-C_5 alkyl group.

2. The composition of claim 1, wherein the basefuel is a wide boiling range alkylate.

3. The composition of claim 1, wherein the alkyl tertiary butyl ether is methyl tertiary butyl ether.

4. The composition of claim 1, wherein the alkyl tertiary butyl ether is ethyl tertiary butyl ether.

5. The composition of claim 1, wherein the aromatic amine is analine.

6. The composition of claim 1, wherein R_1, R_2, R_3 or R_4 is methyl.

7. The composition of claim 1, wherein the aromatic amine is n-methyl aniline, n-ethyl aniline, m-toluidine, p-toluidine, 3, 5-dimethyl aniline, 4-ethyl aniline or 4-n-butyl aniline.

8. The composition of claim 1, wherein the composition further comprises manganese.

9. The composition of claim 8, wherein the manganese is provided by methyl cyclopentadienyl manganese tricarbonyl.

10. The composition of claim 1, wherein the composition comprises 0.1 to 40 vol% alkyl tertiary butyl ether, 0.1 to 10 wt% aromatic amine and 0 to 0.5 g manganese.

11. The composition of claim 1, wherein the composition comprises 15 to 32 vol% methyl tertiary butyl ether, 1.5 to 6 wt% aniline and 0 to 0.1 g manganese.

12. The composition of claim 1, wherein the composition comprises 15 to 32 vol% ethyl tortiary butyl ether, 1.5 to 6 wt % aniline and 0 to 0.1 g managanese.

13. The composition of claim 1, wherein the MON of the composition is at least 94.

14. The composition of claim 1, wherein the MON of the composition is at least 96.

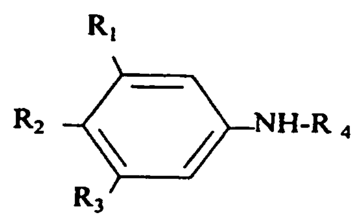
15. The composition of claim 1, wherein the MON of the composition is at least 98.

16. A method for preparing an unleaded aviation fuel composition comprising:

(1) selecting a substantially positive or synergistic combination of

(a) an alkyl tertiary butyl ether, and

(b) an aromatic amine having the formula



wherein R_1, R_2, R_3 and R_4 are hydrogen or a C_1-C_5 alkyl group, and

(2) combining the combination selected in step (1) with an unleaded basefuel.

17. The method of claim 16, wherein the basefuel is a wide boiling range alkylate.

18. The method of claim 16, wherein the alkyl tertiary butyl ether is methyl tertiary butyl ether.

19. The method of claim 16, wherein the alkyl tertiary butyl ether is ethyl tertiary butyl ether.

20. The method of claim 16, wherein the aromatic amine is analine.

21. The method of claim 16, wherein R_1, R_2, R_3 or R_4 is methyl.

22. The method of claim 16, wherein the aromatic amine is n-methyl aniline, n-ethyl aniline, m-toluidine, p-toluidine, 3, 5-dimethyl aniline, 4-ethyl aniline or 4-n-butyl aniline.

23. The method of claim 16, wherein the composition further comprises manganese.

24. The method of claim 23, wherein the manganese is provided by methyl cyclopentadienyl manganese tricarbonyl.

25. The method of claim 16, wherein the composition comprises 0.1 to 40 vol% alkyl tertiary butyl ether, 0.1 to 10 wt% aromatic amine and 0 to 0.5 g manganese.

26. The method of claim 16, wherein the composition comprises 15 to 32 vol% methyl tertiary butyl ether, 1.5 to 6 wt% aniline and 0 to 0.1 g manganese.

27. The method of claim 16, wherein the composition comprises 15 to 32 vol % ethyl tortiary butyl ether, 1.5 to 6 wt % aniline and 0 to 0.1 g maganese.

28. The method of claim 16, wherein the MON of the composition is at least 94.

29. The method of claim 16, wherein the MON of the composition is at least 96.

30. The method of claim 16, wherein the MON of the composition is at least 98.

31. A method for preparing a composition comprising combining a wide boiling range alkylate basefuel and a synergistic amount of alkyl tertiary butyl ether, an aromatic amine and manganese sufficient to raise the motor octane number of the composition to at least 94.

32. The method of claim 31, wherein the synergistic amount is sufficient to raise the motor octane number of the composition to at least 96.

33. The method of claim 31, wherein the synergistic amount is sufficient to raise the motor octane number of the composition to at least 98.

34. A method for operating a piston driven aircraft which comprises operating the aircraft engine with the aviation fuel composition of claim 1.

35. A method for operating a piston driven aircraft which comprises operating the aircraft engine with the aviation fuel composition made by the method of claim 29.

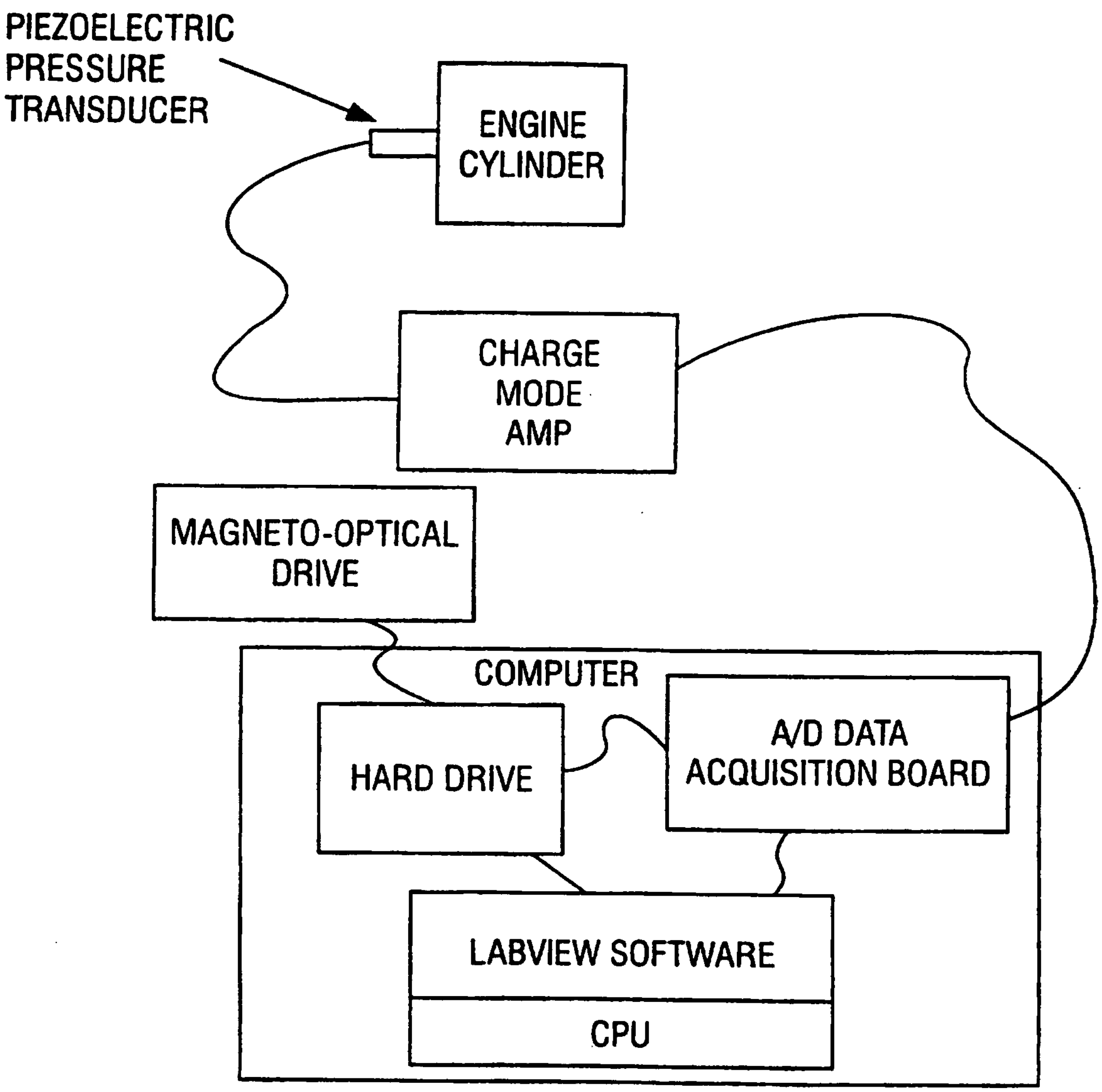

PIEZOELECTRIC
PRESSURE
TRANSDUCER
ENGINE
CYLINDER
CHARGE
MODE
AMP
MAGNETO-OPTICAL
DRIVE
COMPUTER
HARD DRIVE
A/D DATA
ACQUISITION BOARD
LABVIEW SOFTWARE
CPU

FIG. 1

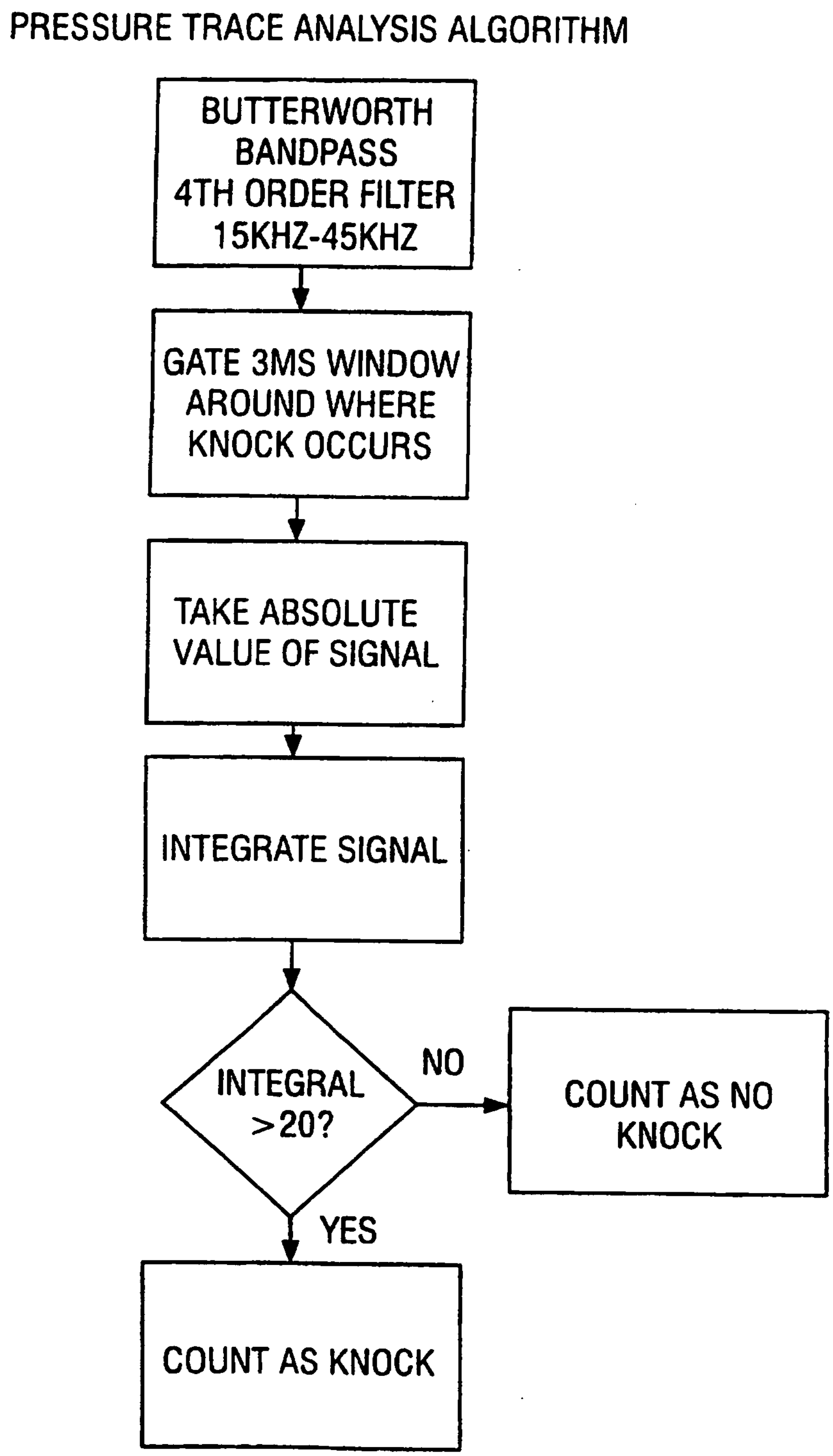

PRESSURE TRACE ANALYSIS ALGORITHM
BUTTERWORTH BANDPASS 4TH ORDER FILTER 15KHZ-45KHZ
GATE 3MS WINDOW AROUND WHERE KNOCK OCCURS
TAKE ABSOLUTE VALUE OF SIGNAL
INTEGRATE SIGNAL
INTEGRAL >20?
NO
COUNT AS NO KNOCK
YES
COUNT AS KNOCK

FIG. 2

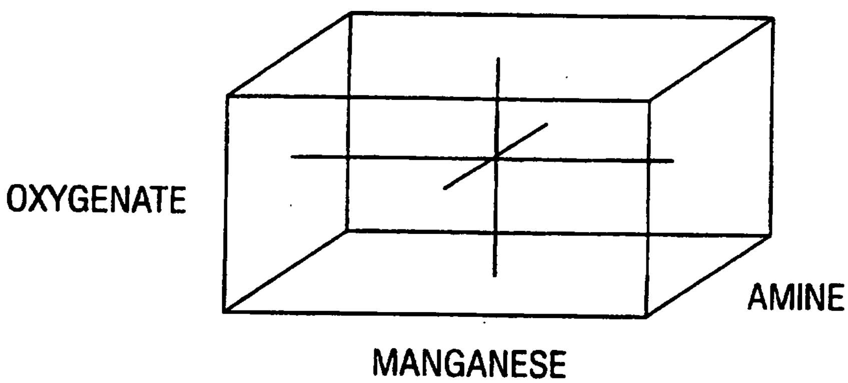


FIG. 3

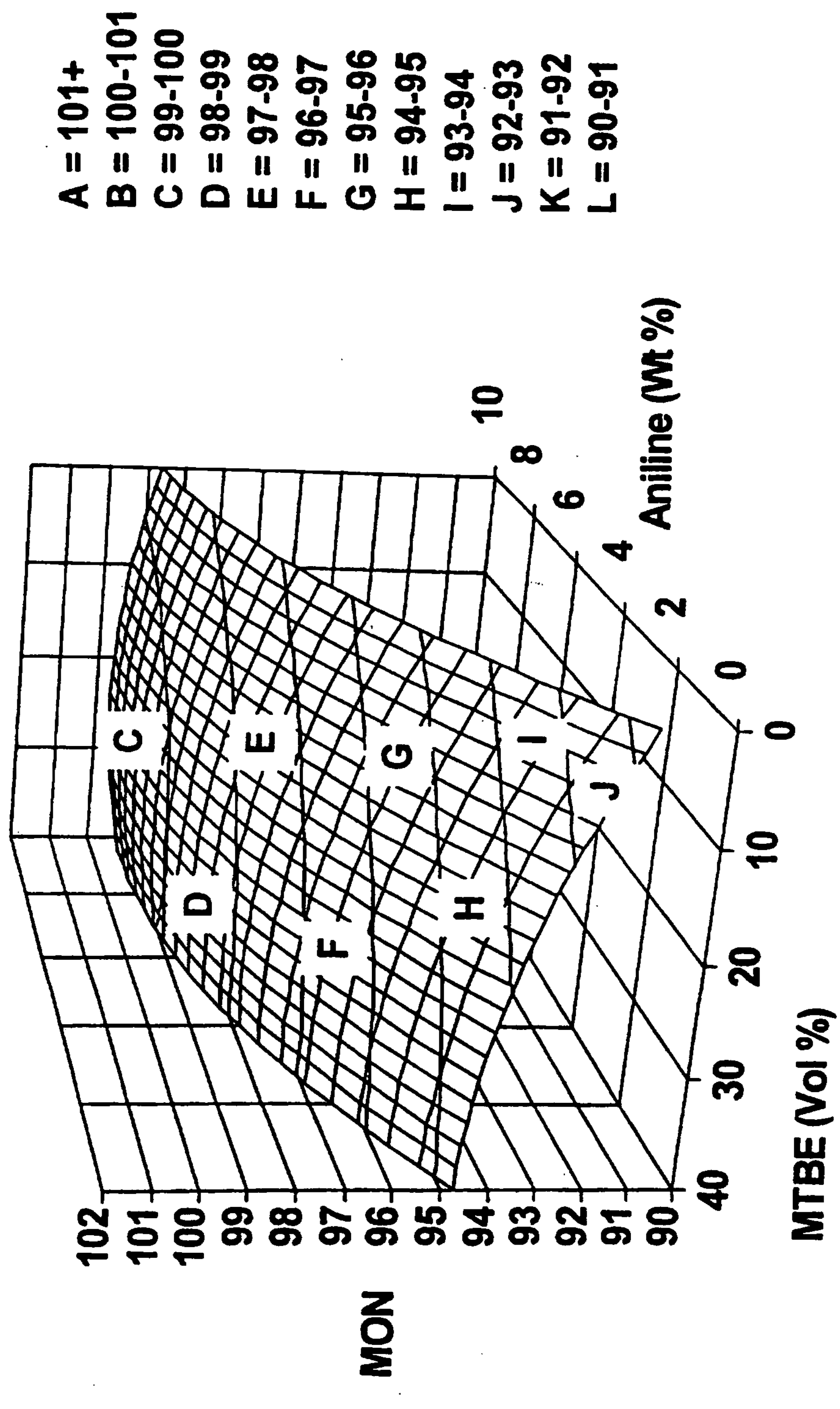

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102
101
100
99
98
97
96
95
94
93
92
91
90
MTBE (Vol %)
40
30
20
10
0
Aniline (Wt %)
0
2
4
6
8
10
C
D
E
F
G
H
I
J

FIG. 4

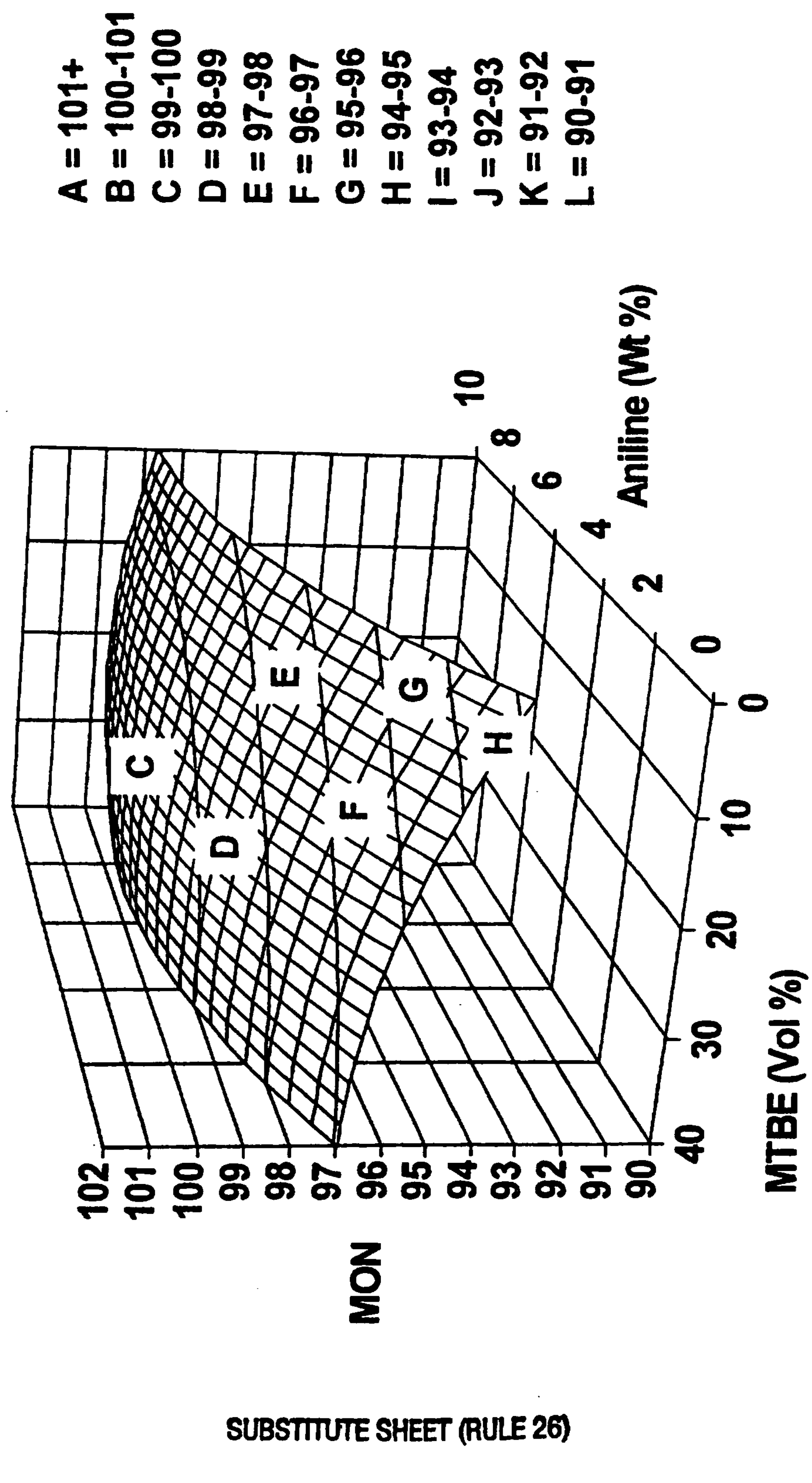

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102
101
100
99
98
97
96
95
94
93
92
91
90
MTBE (Vol %)
40
30
20
10
0
Aniline (Wt %)
0
2
4
6
8
10
C
D
E
F
G
H

FIG. 5

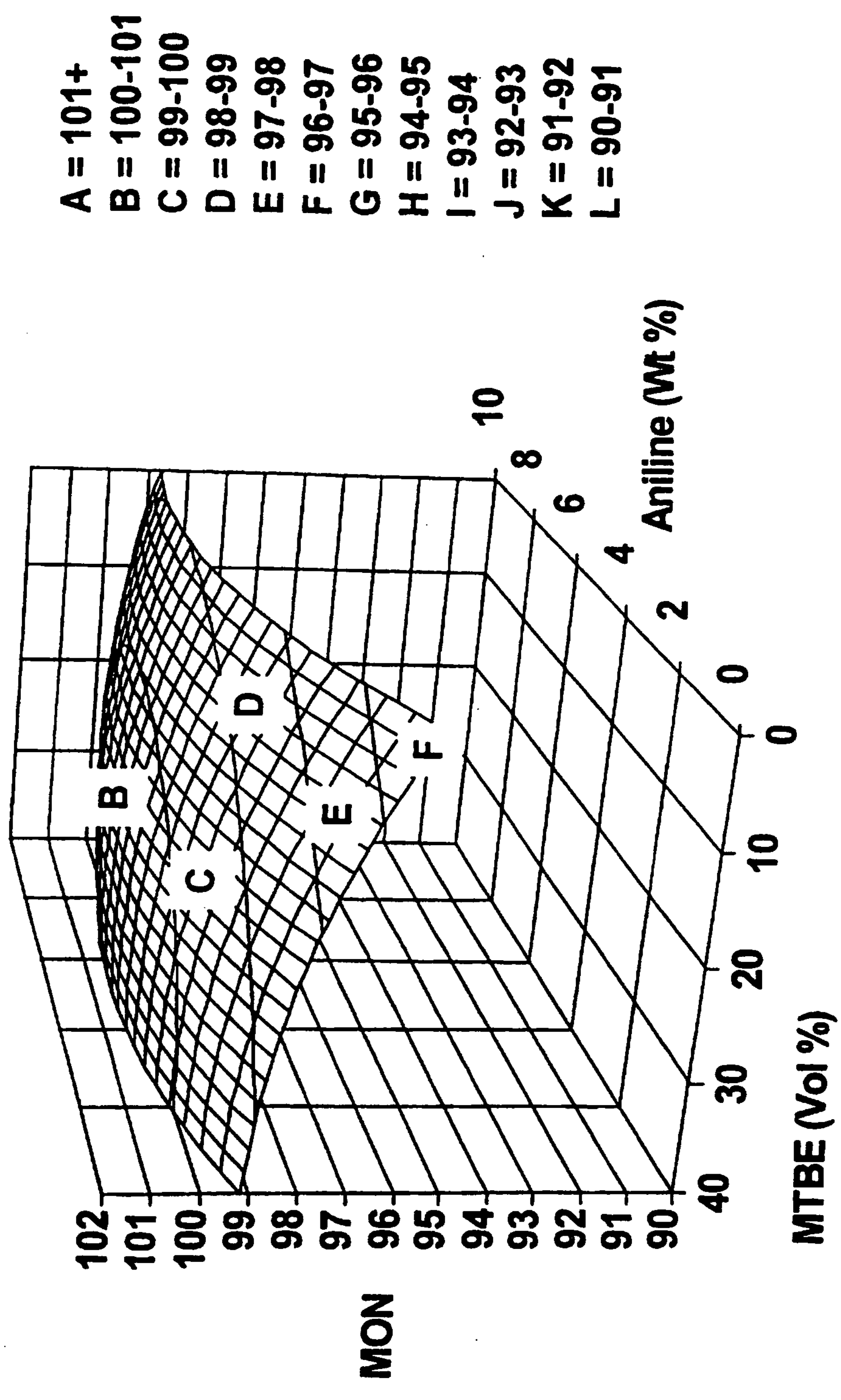

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102 101 100 99 98 97 96 95 94 93 92 91 90
MTBE (Vol %)
40 30 20 10 0
Aniline (Wt %)
0 2 4 6 8 10
A B C D E F

FIG. 6

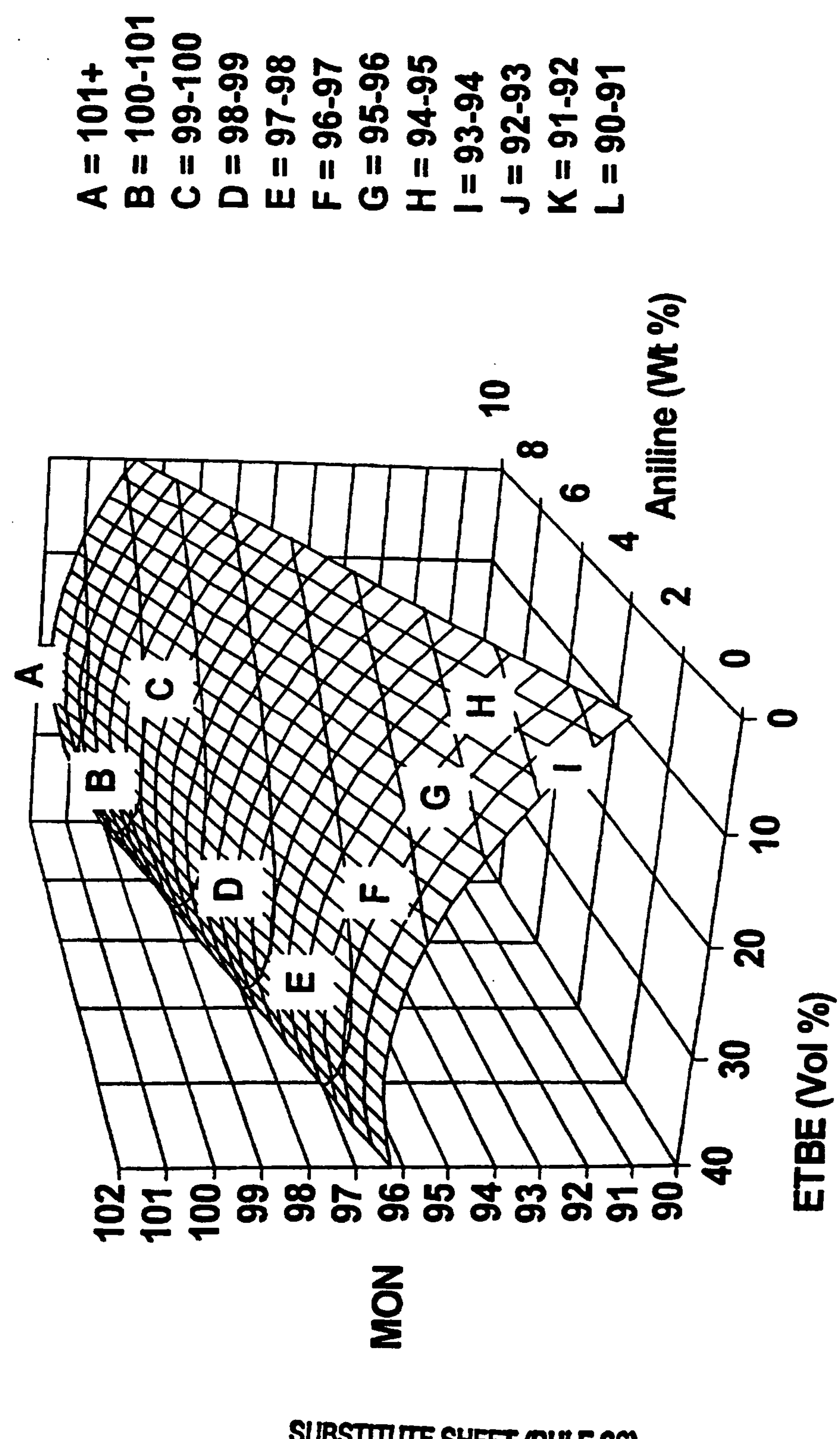

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102
101
100
99
98
97
96
95
94
93
92
91
90
ETBE (Vol %)
40
30
20
10
0
Aniline (Wt %)
0
2
4
6
8
10
A
B
C
D
E
F
G
H
I

FIG. 7

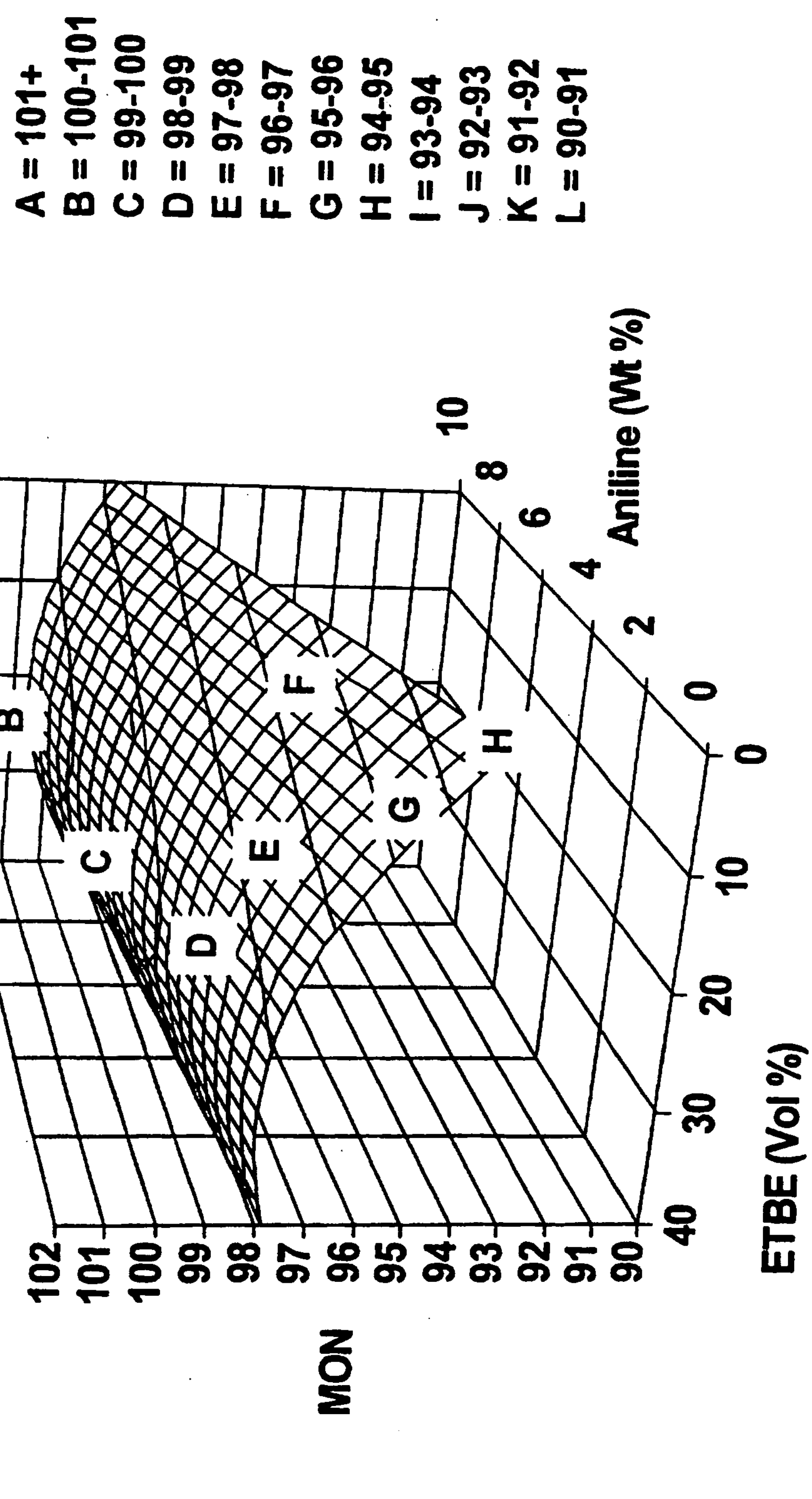

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102
101
100
99
98
97
96
95
94
93
92
91
90
ETBE (Vol %)
40
30
20
10
0
Aniline (Wt %)
0
2
4
6
8
10
B
C
D
E
F
G
H

FIG. 8

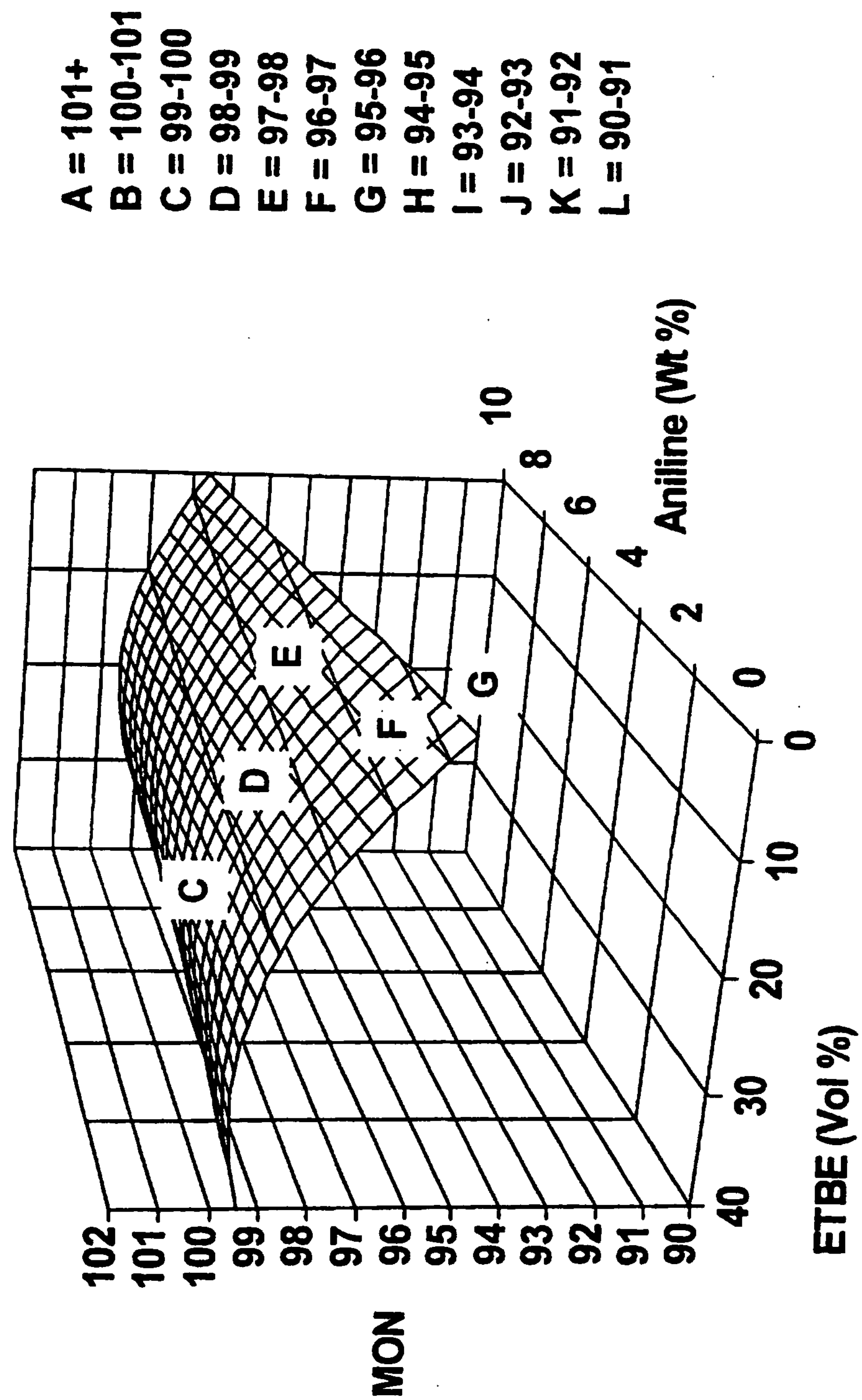

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102
101
100
99
98
97
96
95
94
93
92
91
90
ETBE (Vol %)
40
30
20
10
0
Aniline (Wt %)
0
2
4
6
8
10
C
D
E
F
G

FIG. 9

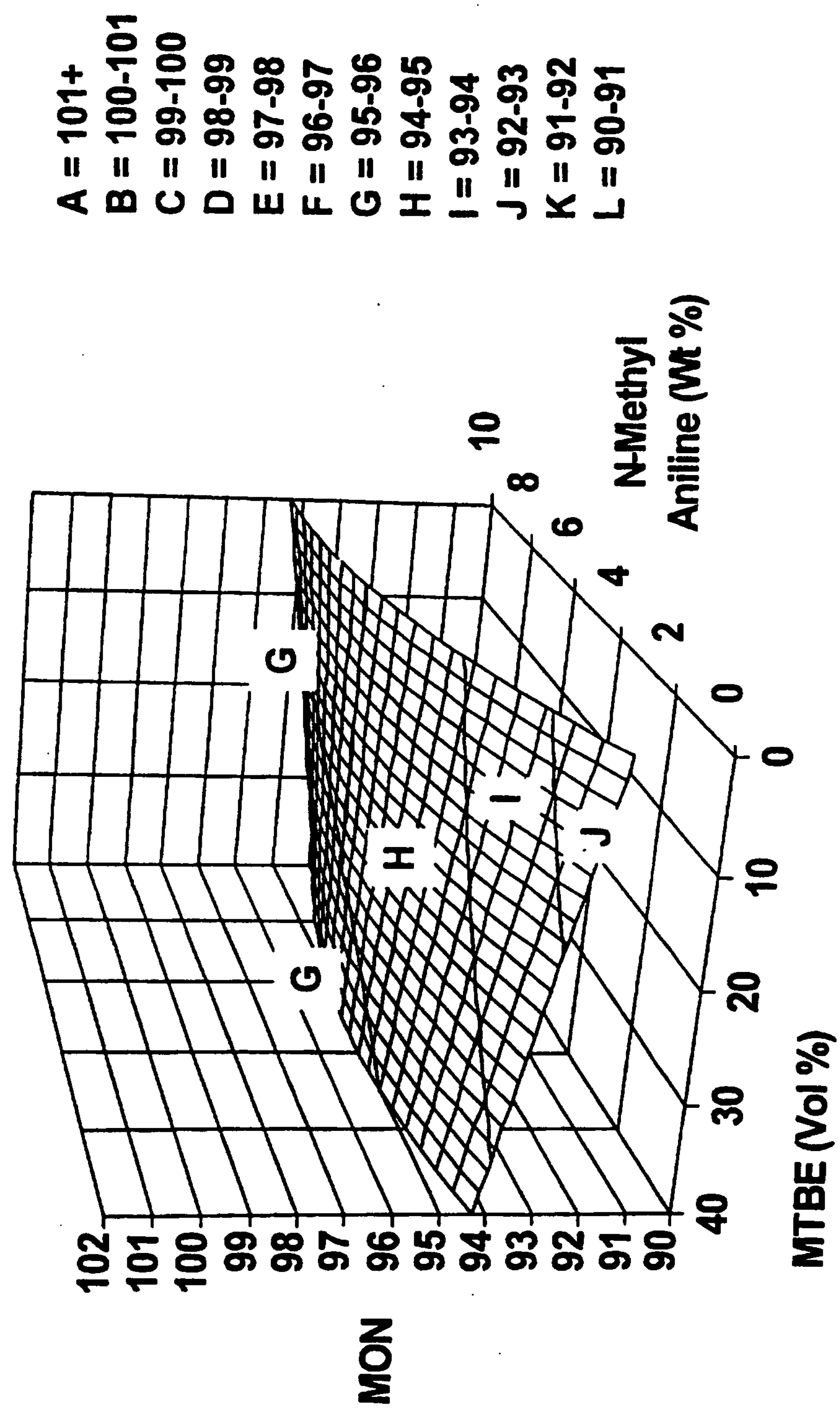

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102
101
100
99
98
97
96
95
94
93
92
91
90
MTBE (Vol %)
40
30
20
10
0
N-Methyl Aniline (Wt %)
0
2
4
6
8
10
G
H
I
J
G

FIG. 10

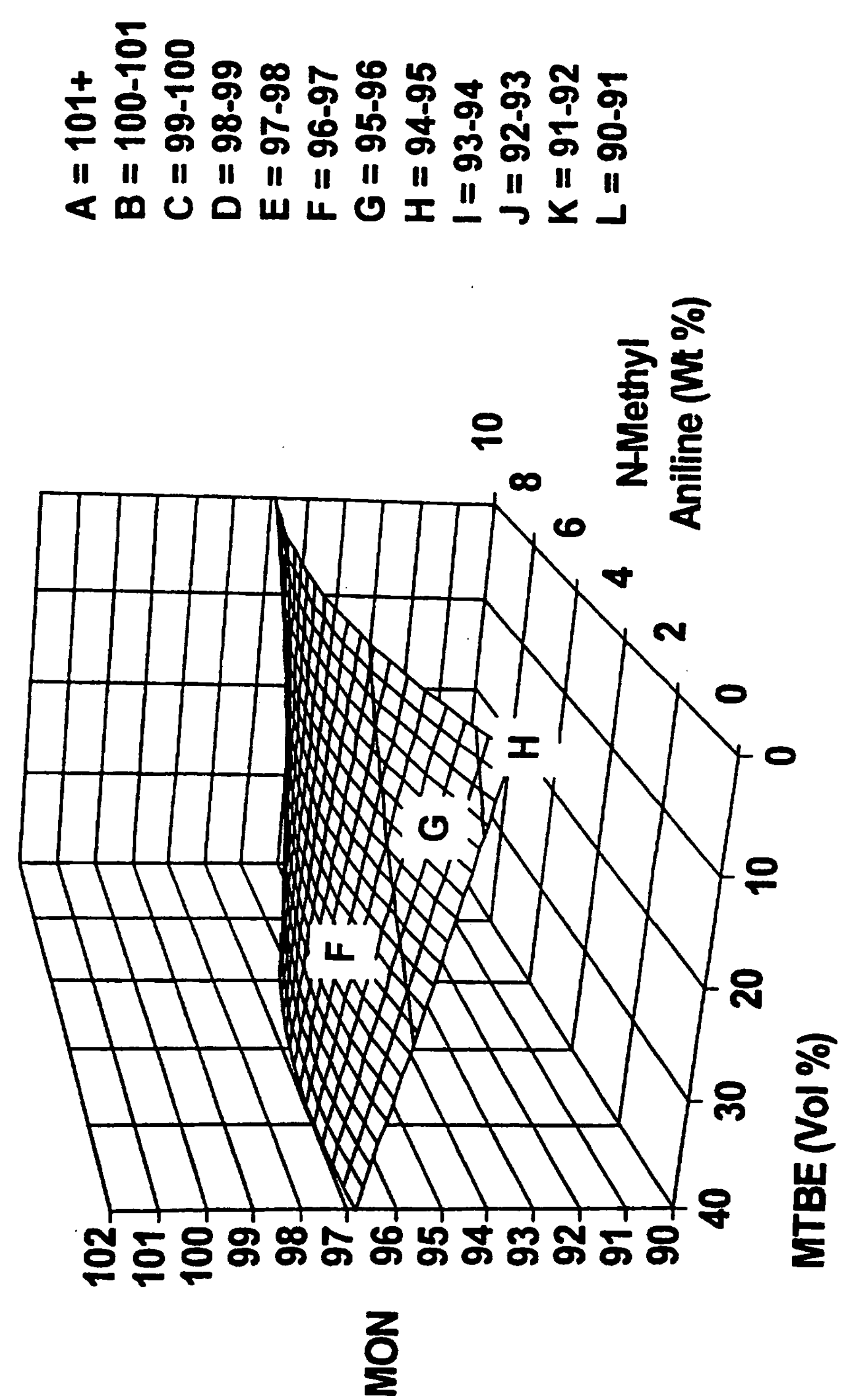

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102
101
100
99
98
97
96
95
94
93
92
91
90
MTBE (Vol %)
0
10
20
30
40
N-Methyl Aniline (Wt %)
0
2
4
6
8
10
F
G
H

FIG. 11

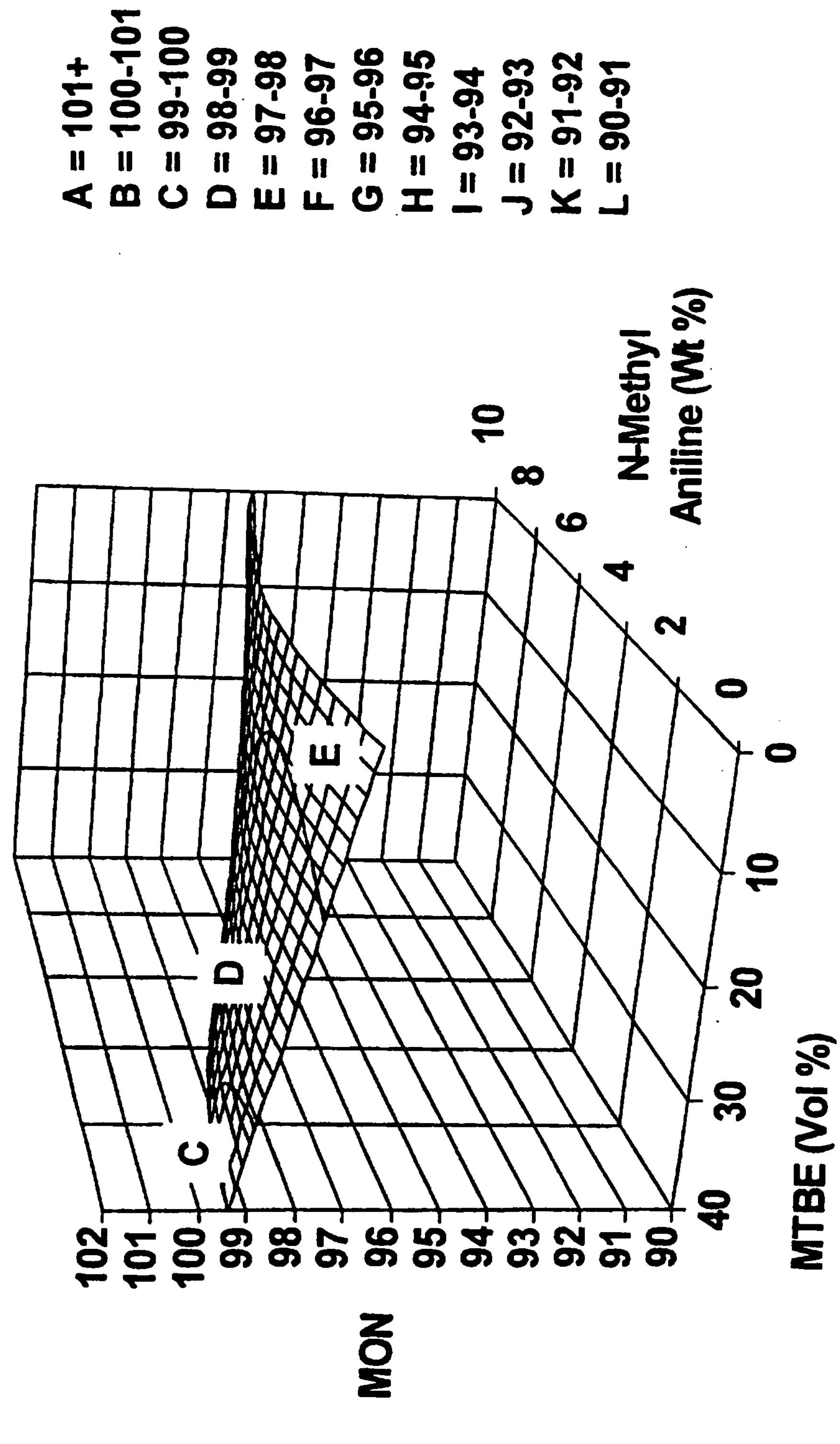

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102
101
100
99
98
97
96
95
94
93
92
91
90
MTBE (Vol %)
40
30
20
10
0
N-Methyl Aniline (Wt %)
0
2
4
6
8
10
C
D
E

FIG. 12

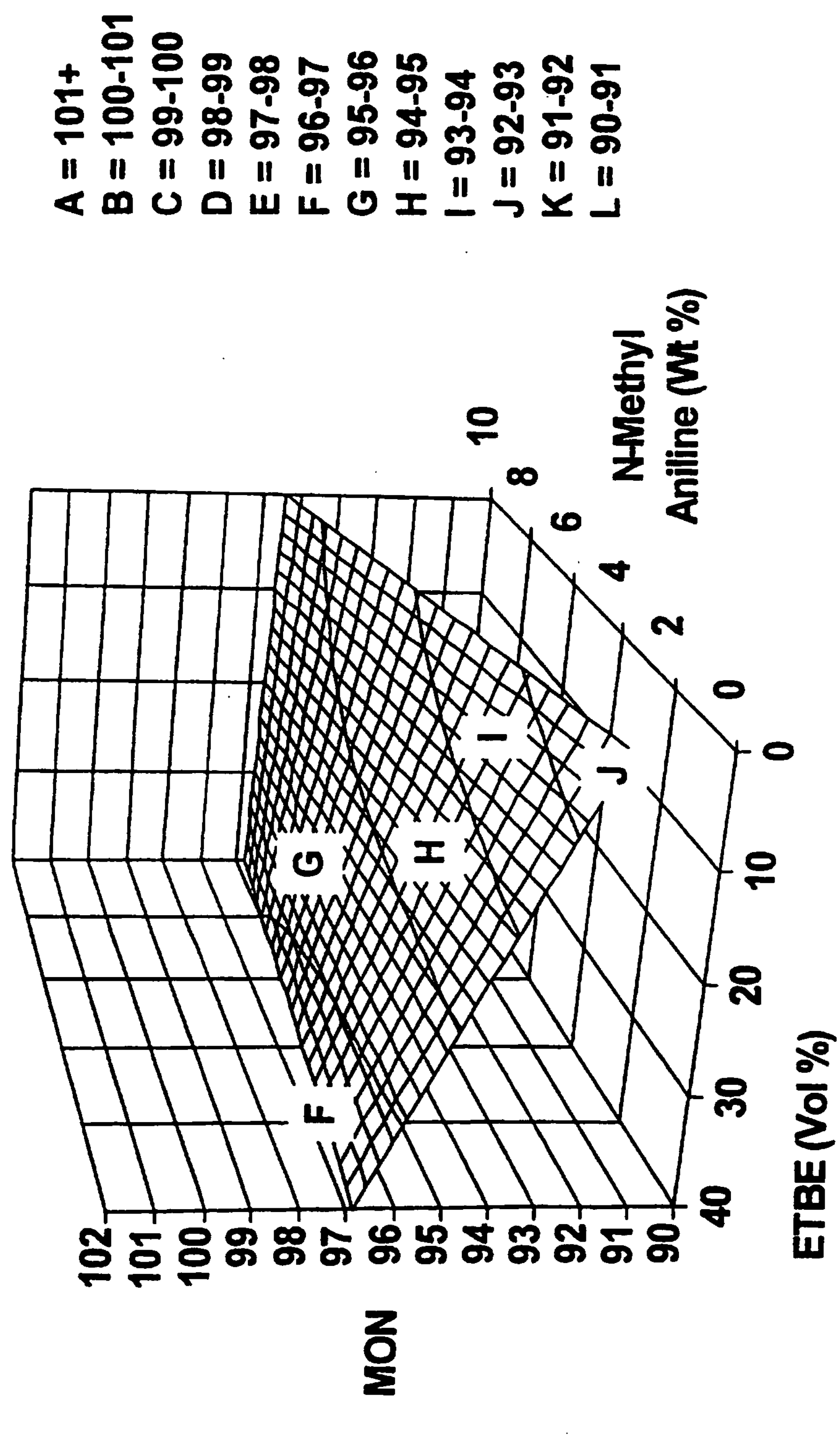

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102
101
100
99
98
97
96
95
94
93
92
91
90
ETBE (Vol %)
40
30
20
10
0
N-Methyl Aniline (Wt %)
0
2
4
6
8
10
F
G
H
I
J

FIG. 13

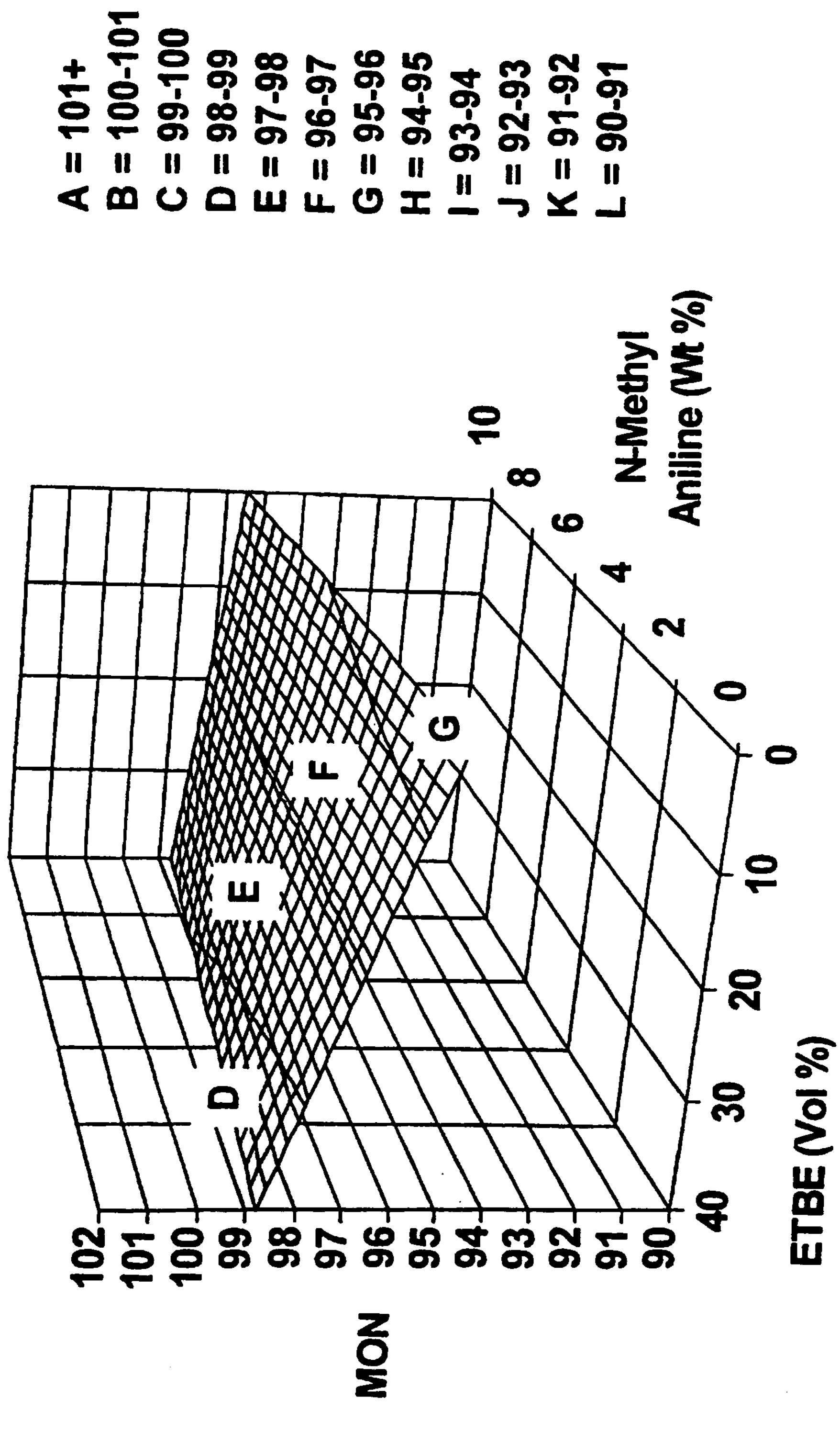

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102
101
100
99
98
97
96
95
94
93
92
91
90
ETBE (Vol %)
40
30
20
10
0
N-Methyl Aniline (Wt %)
0
2
4
6
8
10
D
E
F
G

FIG. 14

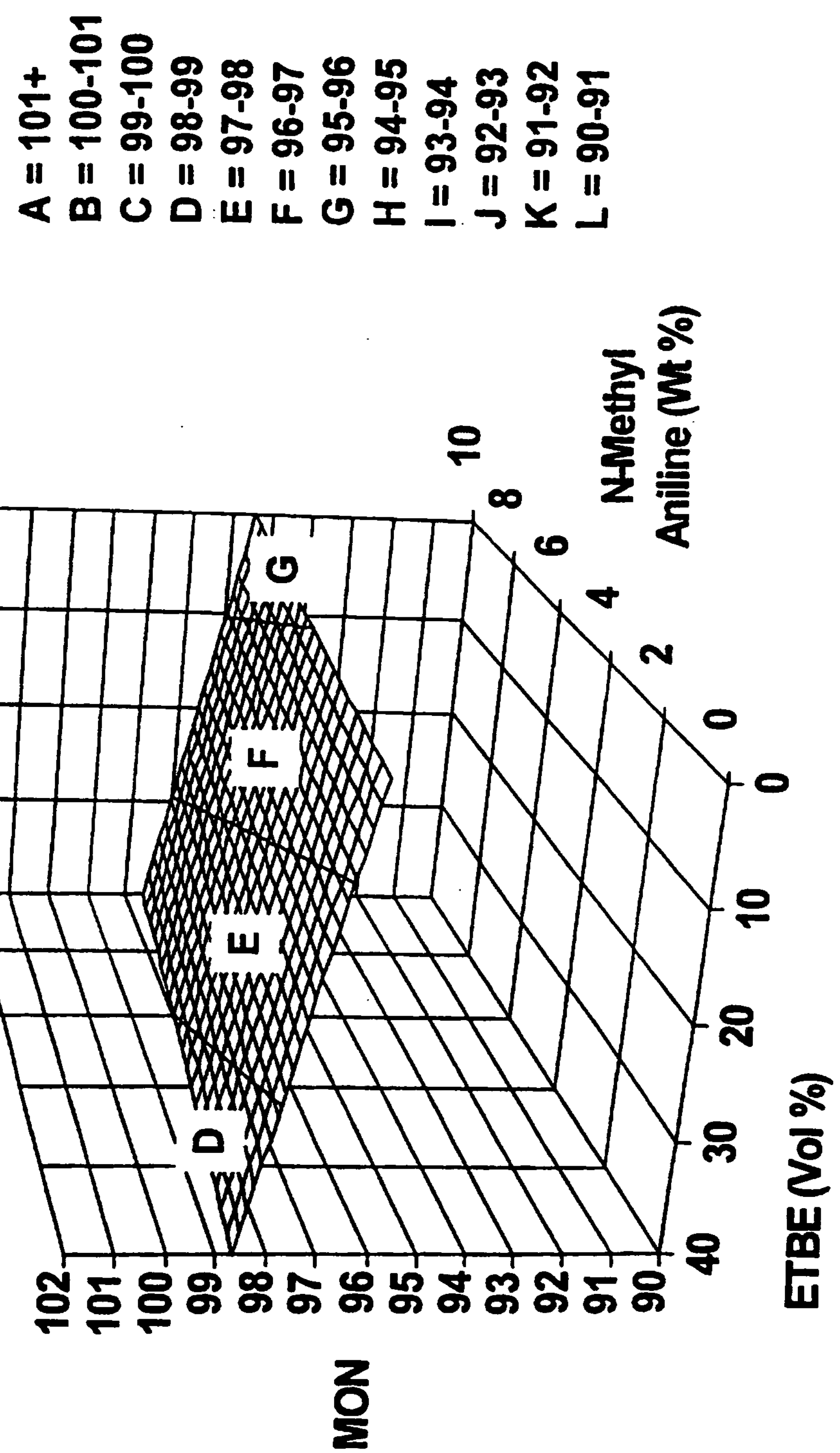

A = 101+
B = 100-101
C = 99-100
D = 98-99
E = 97-98
F = 96-97
G = 95-96
H = 94-95
I = 93-94
J = 92-93
K = 91-92
L = 90-91
MON
102
101
100
99
98
97
96
95
94
93
92
91
90
ETBE (Vol %)
40
30
20
10
0
0
2
4
6
8
10
N-Methyl Aniline (Wt %)
D
E
F
G

FIG. 15

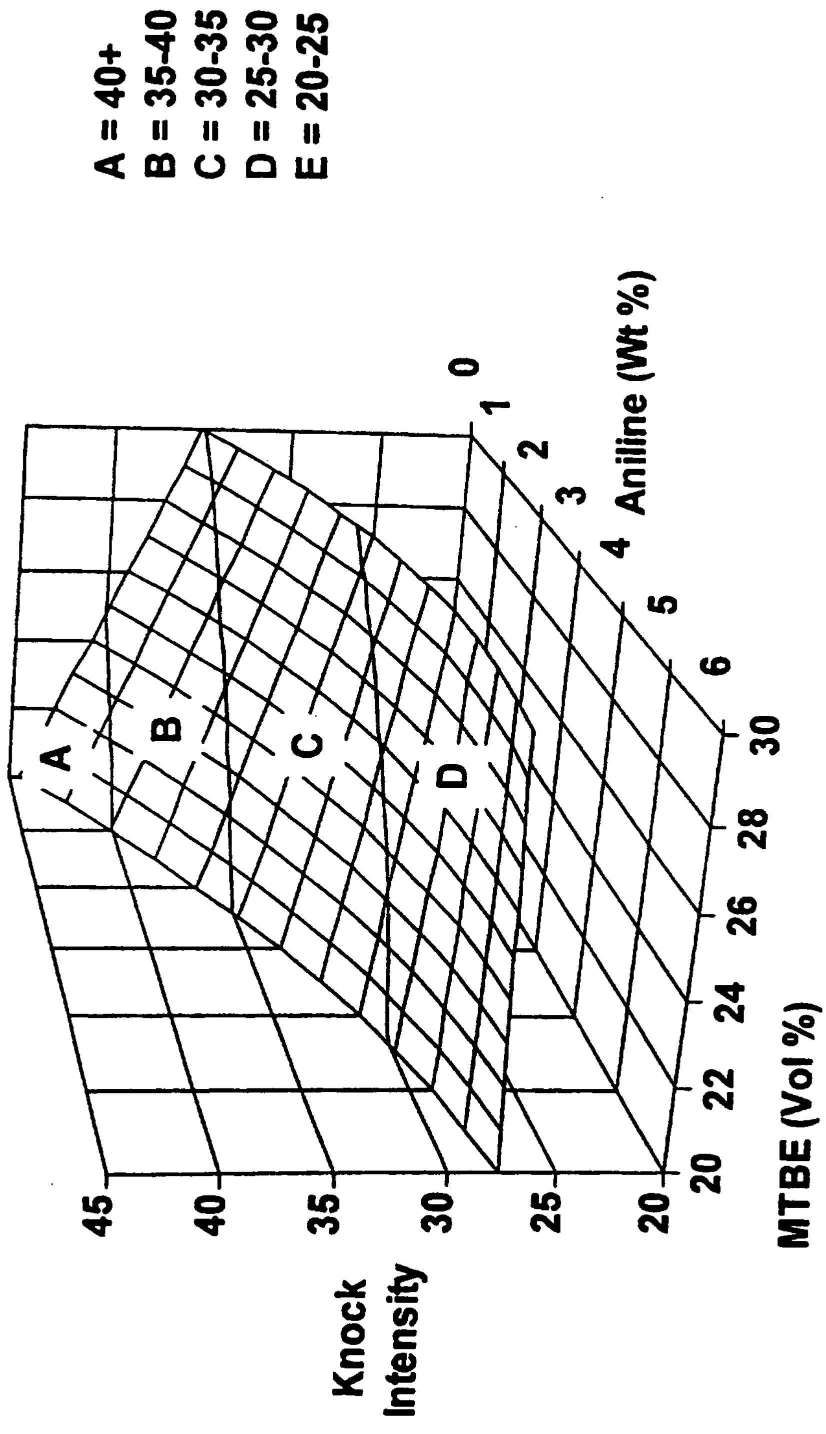

A = 40+
B = 35-40
C = 30-35
D = 25-30
E = 20-25
Knock Intensity
45
40
35
30
25
20
MTBE (Vol %)
20
22
24
26
28
30
Aniline (Wt %)
0
1
2
3
4
5
6
A
B
C
D

FIG. 16

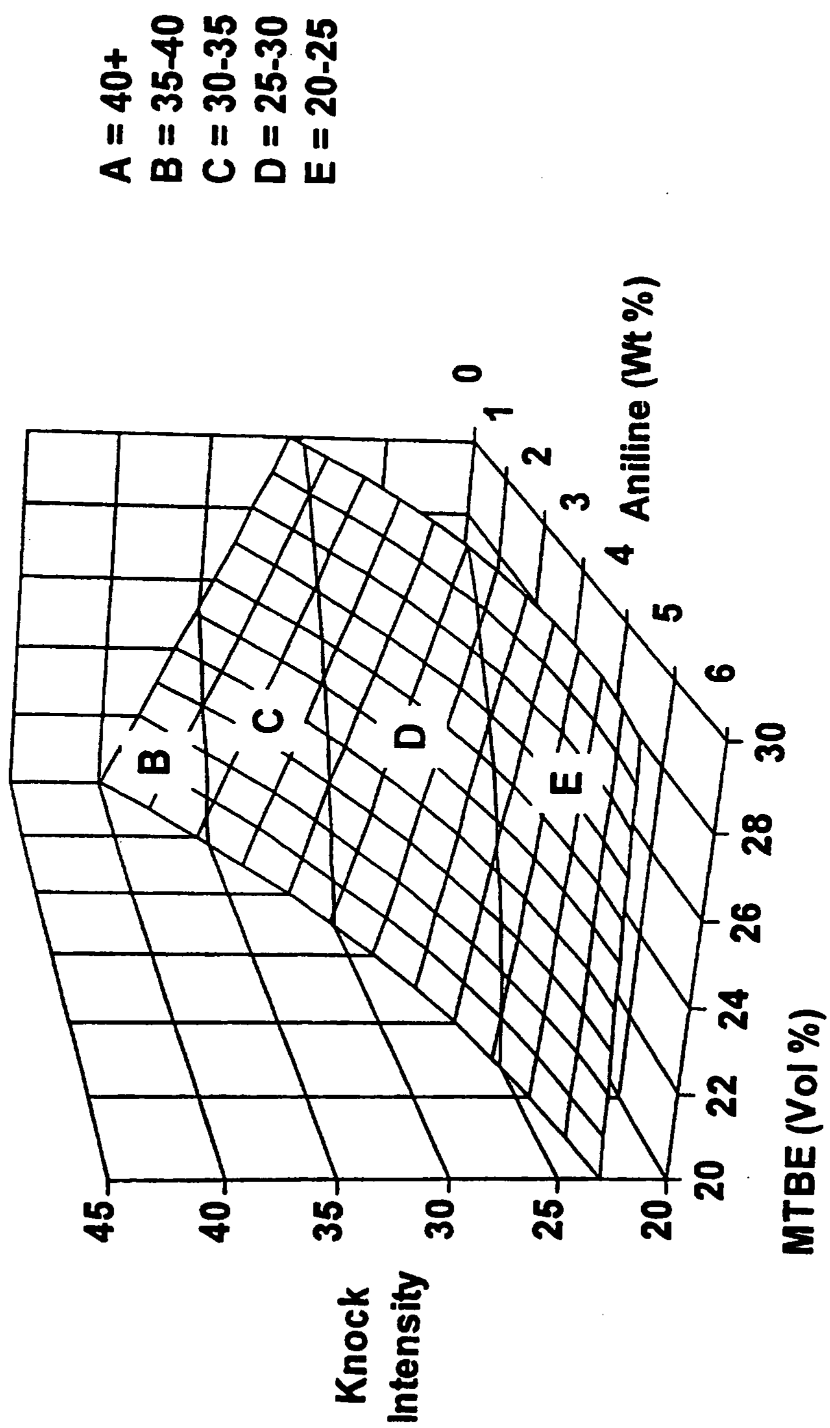

A = 40+
B = 35-40
C = 30-35
D = 25-30
E = 20-25
Aniline (Wt %)
0
1
2
3
4
5
6
MTBE (Vol %)
20
22
24
26
28
30
Knock Intensity
20
25
30
35
40
45
A
B
C
D
E

FIG. 17

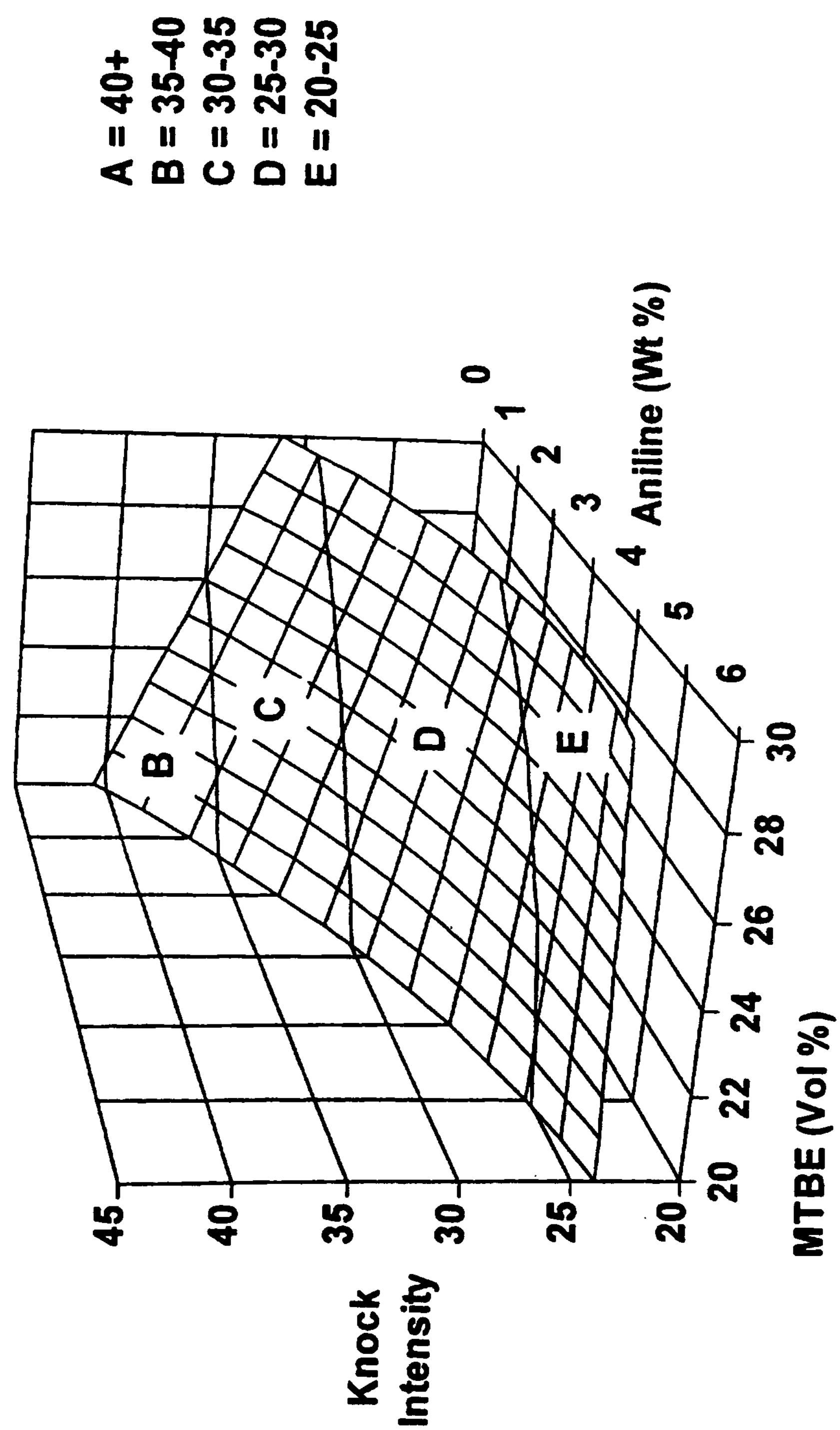

A = 40+
B = 35-40
C = 30-35
D = 25-30
E = 20-25
Knock Intensity
45
40
35
30
25
20
MTBE (Vol %)
20
22
24
26
28
30
Aniline (Wt %)
0
1
2
3
4
5
6
A
B
C
D
E

FIG. 18

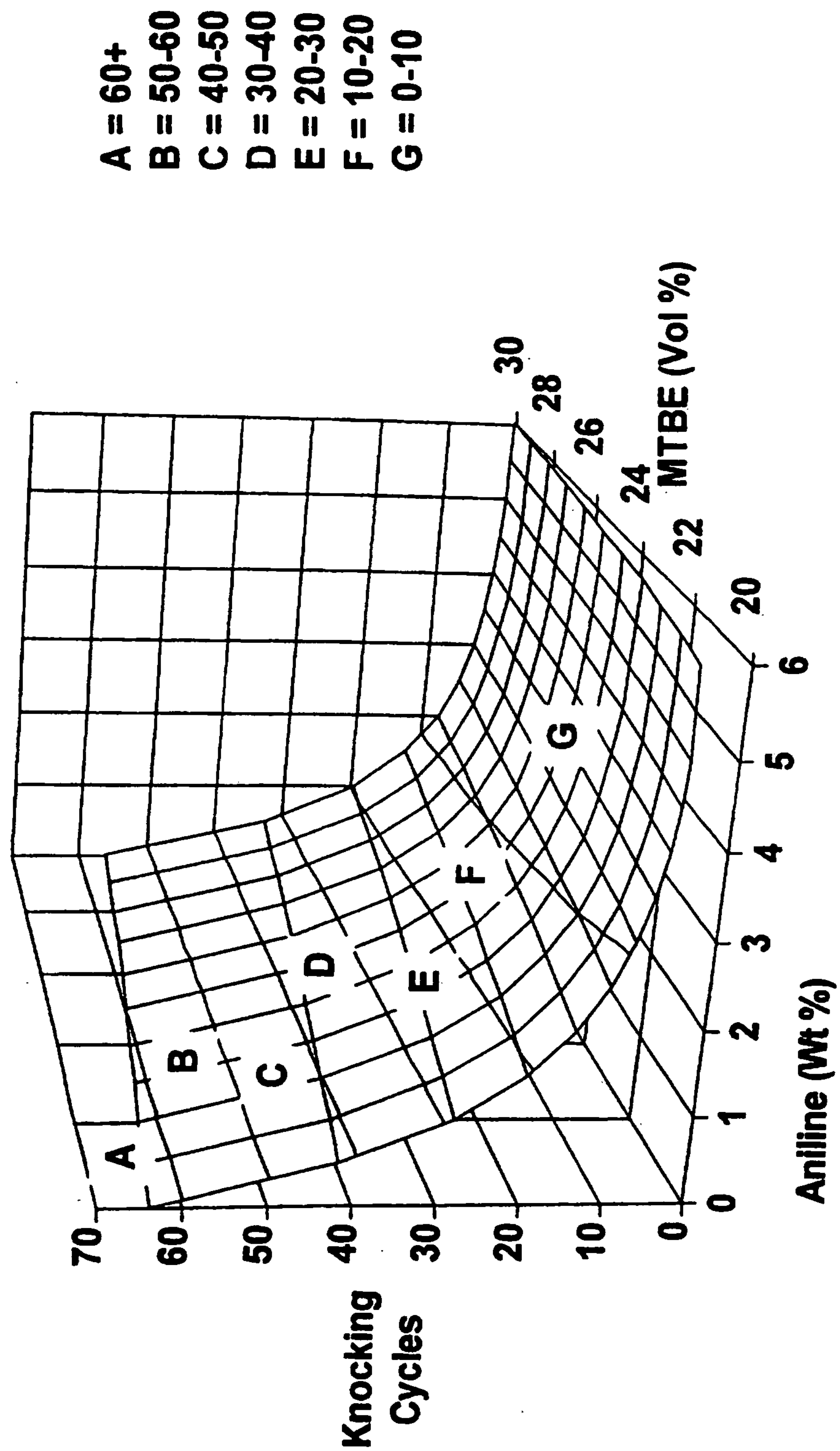

A = 60+
B = 50-60
C = 40-50
D = 30-40
E = 20-30
F = 10-20
G = 0-10
Knocking Cycles
0
10
20
30
40
50
60
70
Aniline (Wt %)
0
1
2
3
4
5
6
MTBE (Vol %)
20
22
24
26
28
30
A
B
C
D
E
F
G

FIG. 19

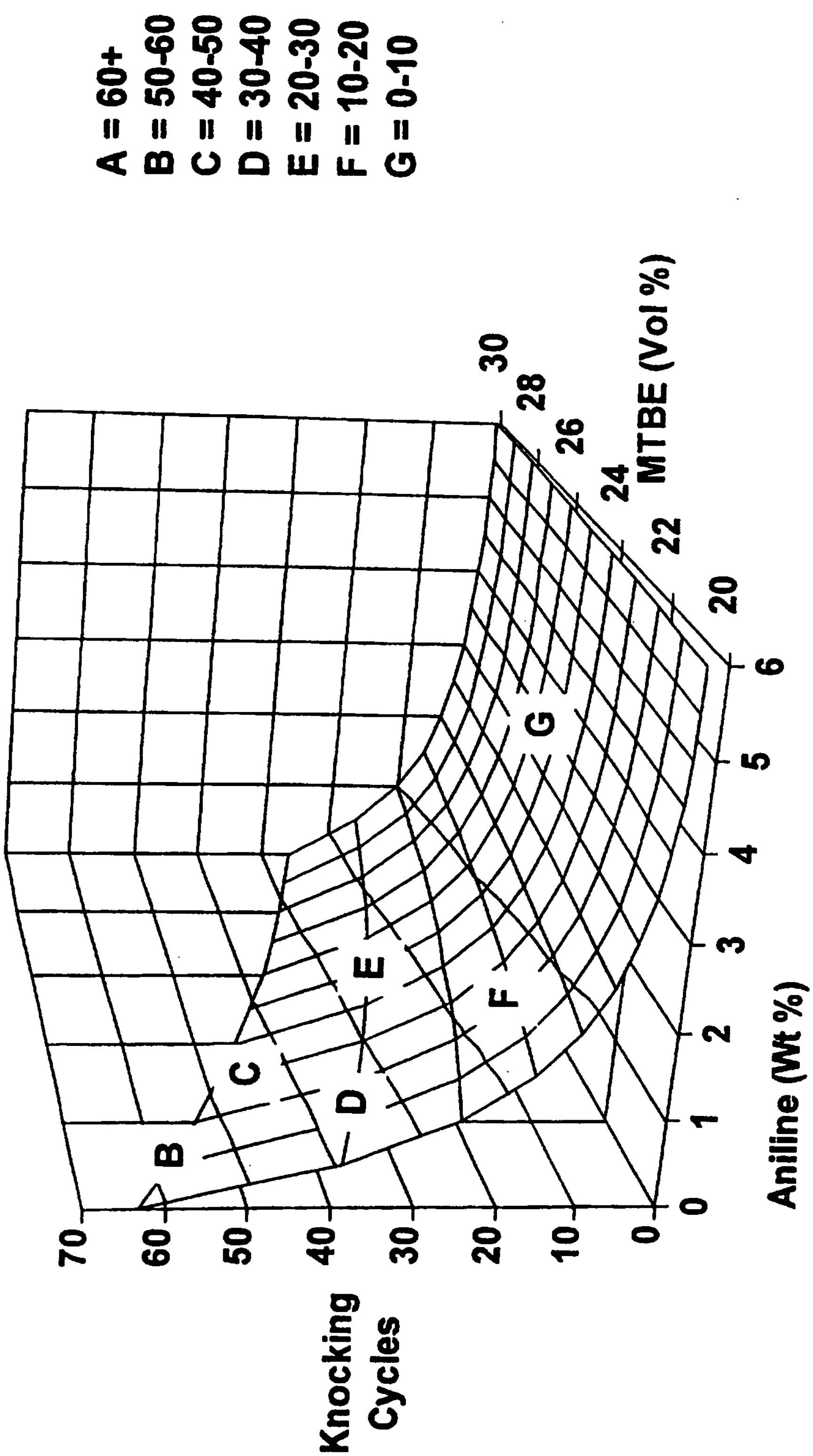

A = 60+
B = 50-60
C = 40-50
D = 30-40
E = 20-30
F = 10-20
G = 0-10
Knocking Cycles
70
60
50
40
30
20
10
0
Aniline (Wt %)
0
1
2
3
4
5
6
MTBE (Vol %)
20
22
24
26
28
30
A
B
C
D
E
F
G

FIG. 20

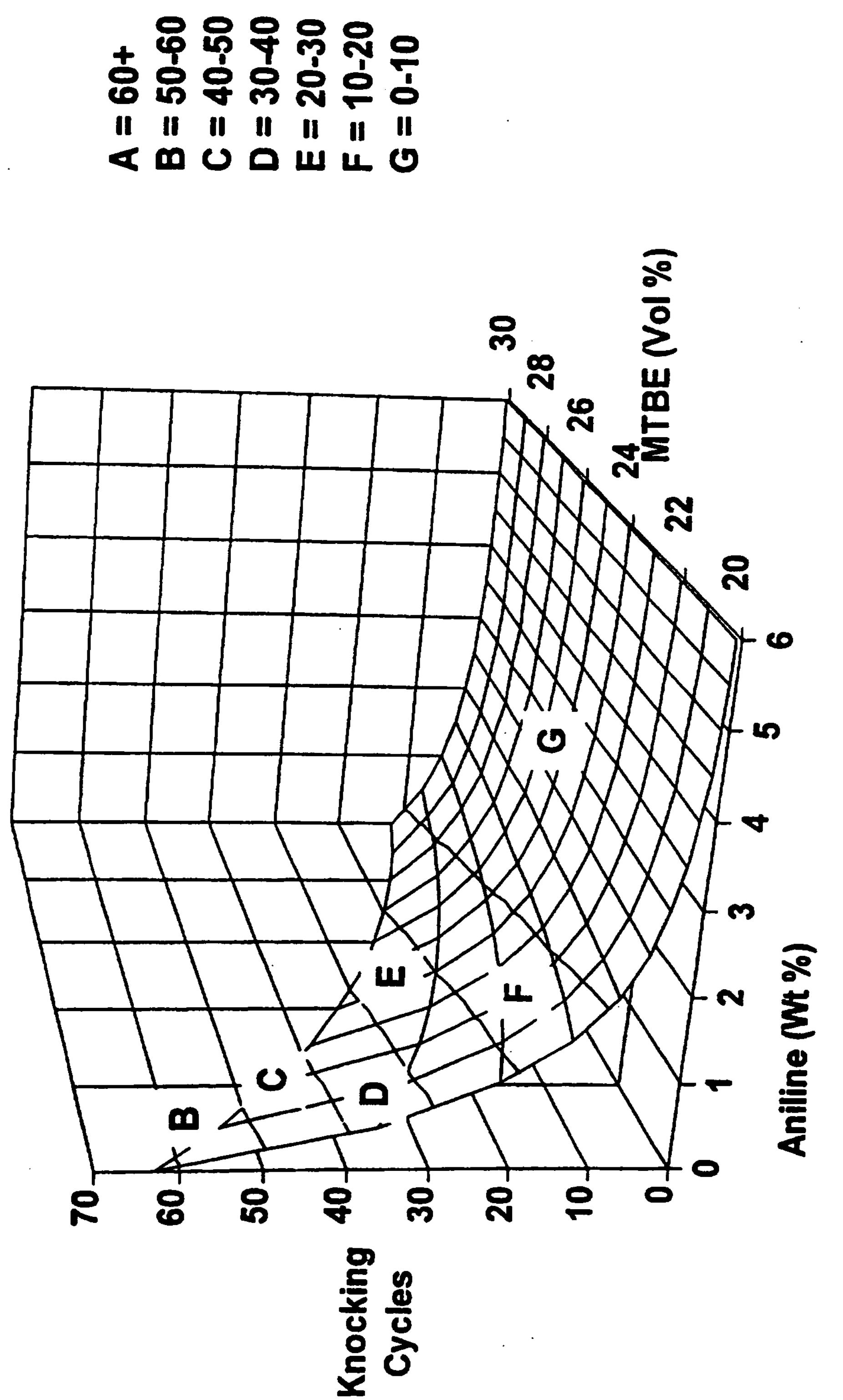

A = 60+
B = 50-60
C = 40-50
D = 30-40
E = 20-30
F = 10-20
G = 0-10
Knocking Cycles
70
60
50
40
30
20
10
0
Aniline (Wt %)
0
1
2
3
4
5
6
MTBE (Vol %)
20
22
24
26
28
30
A
B
C
D
E
F
G

FIG. 21

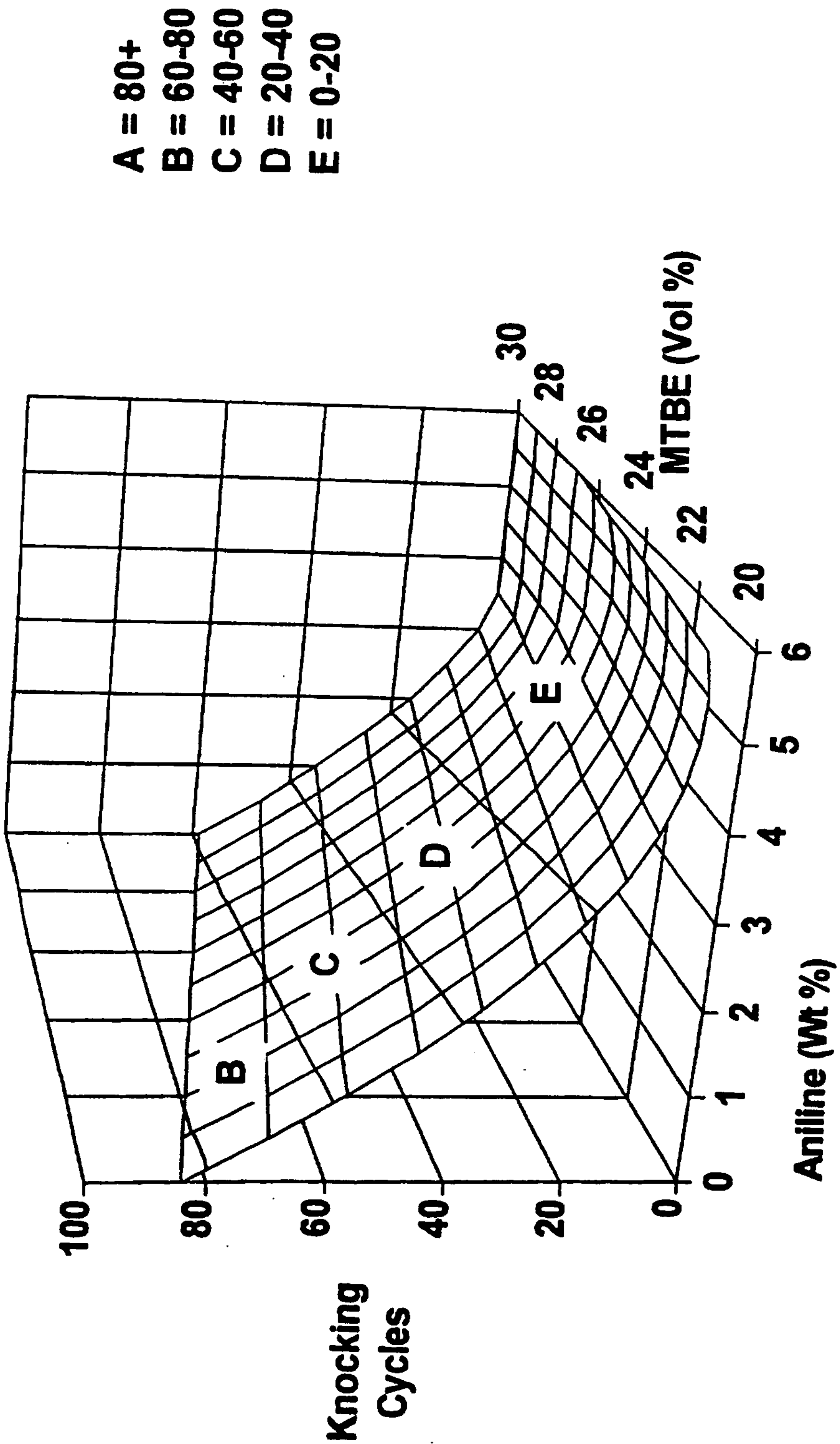

A = 80+
B = 60-80
C = 40-60
D = 20-40
E = 0-20
Knocking Cycles
100
80
60
40
20
0
Aniline (Wt %)
0
1
2
3
4
5
6
MTBE (Vol %)
20
22
24
26
28
30
A
B
C
D
E

FIG. 22

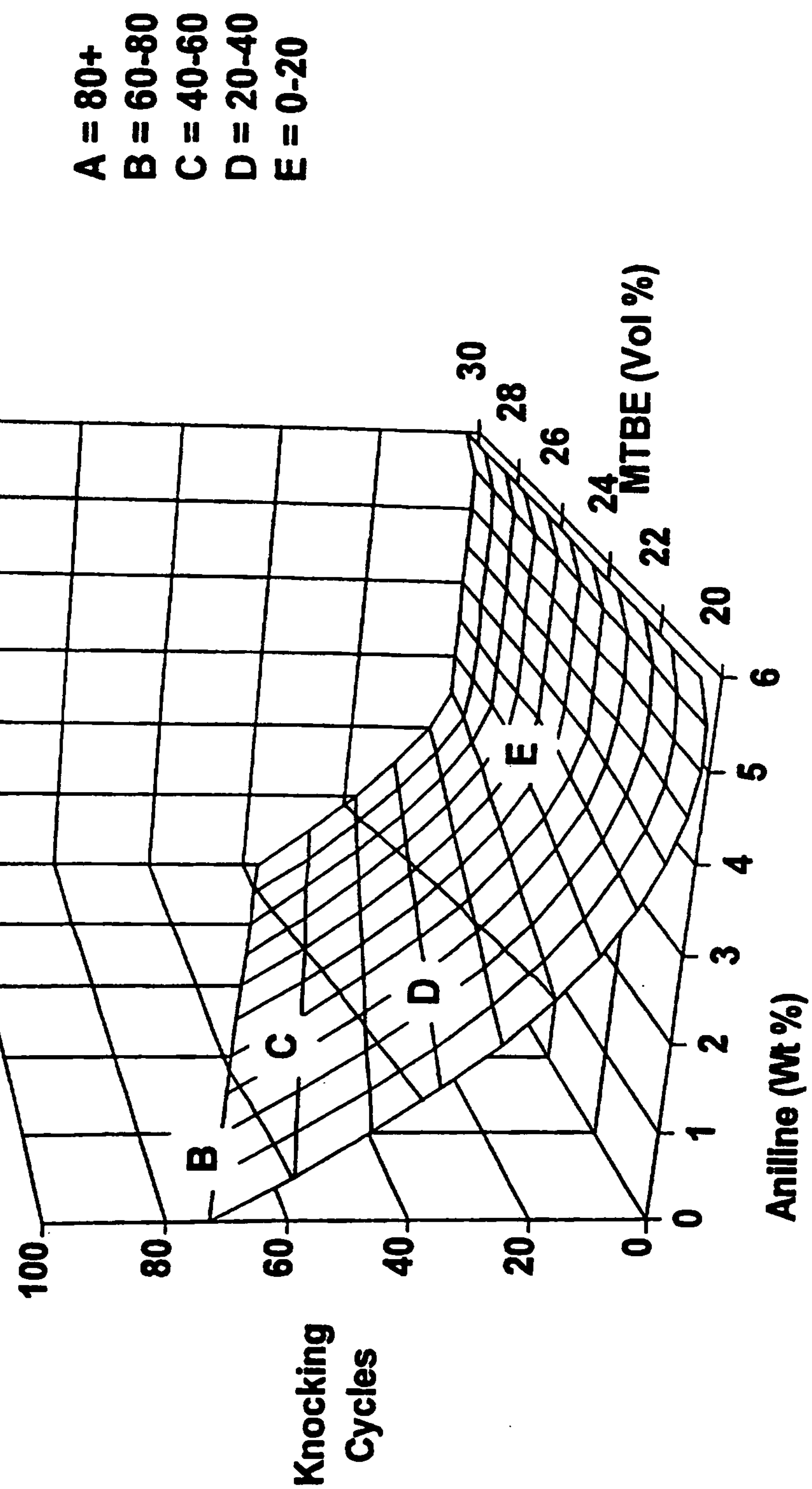

A = 80+
B = 60-80
C = 40-60
D = 20-40
E = 0-20
Knocking Cycles
100
80
60
40
20
0
Aniline (Wt %)
0
1
2
3
4
5
6
MTBE (Vol %)
20
22
24
26
28
30
B
C
D
E

FIG. 23

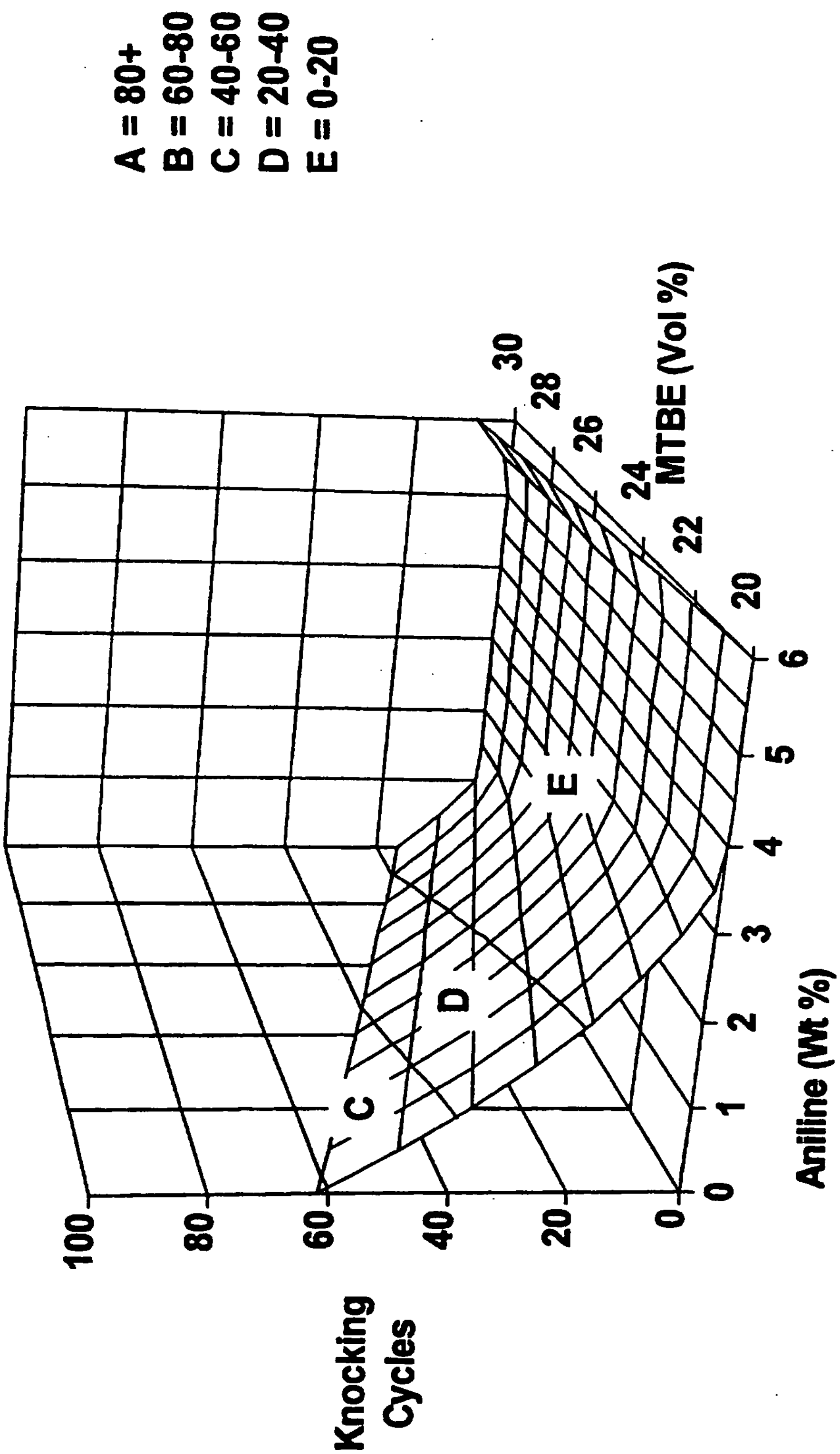

A = 80+
B = 60-80
C = 40-60
D = 20-40
E = 0-20
Knocking Cycles
100
80
60
40
20
0
Aniline (Wt %)
0
1
2
3
4
5
6
MTBE (Vol %)
20
22
24
26
28
30
C
D
E

FIG. 24

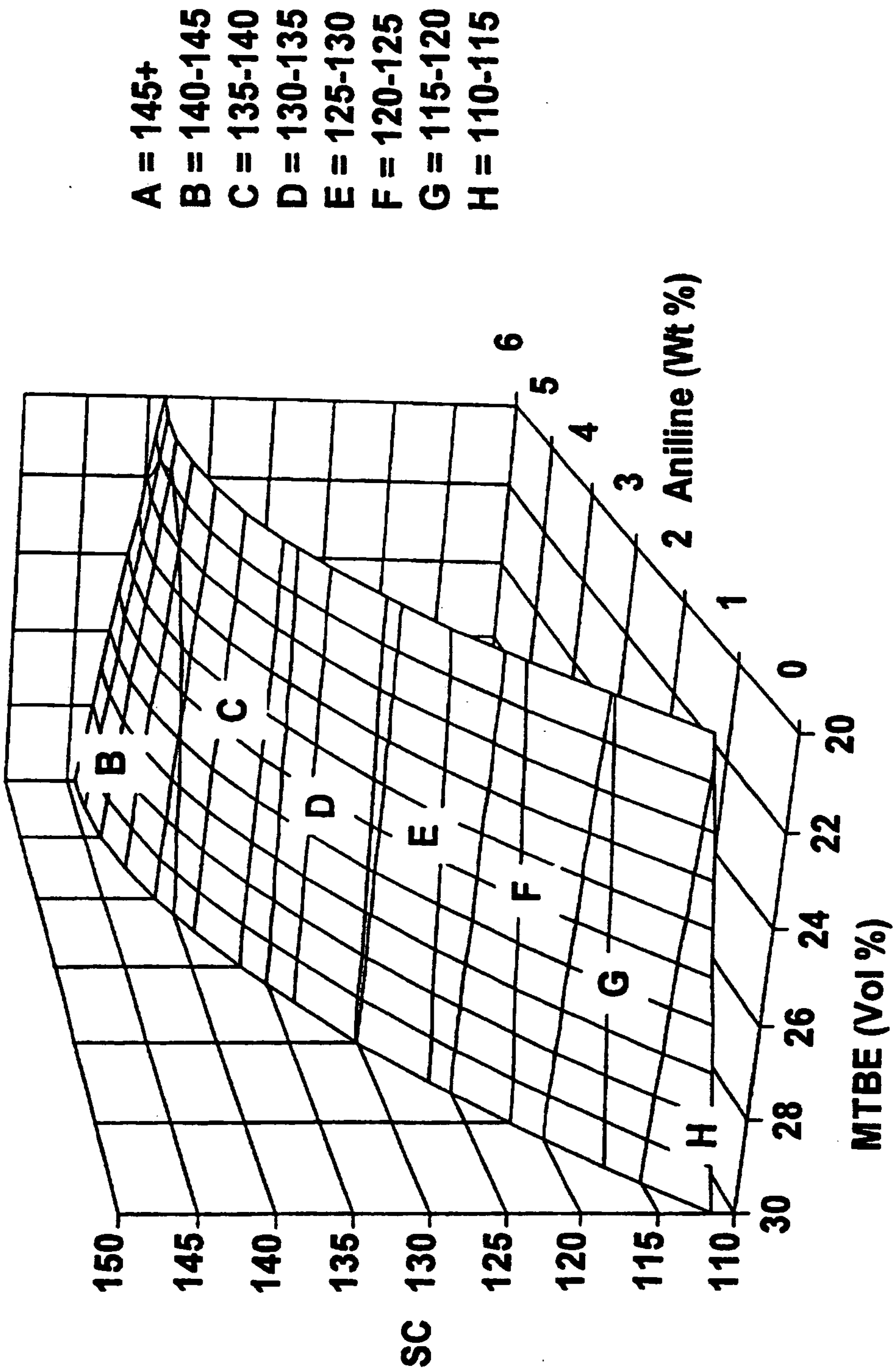

A = 145+
B = 140-145
C = 135-140
D = 130-135
E = 125-130
F = 120-125
G = 115-120
H = 110-115
SC
150
145
140
135
130
125
120
115
110
MTBE (Vol %)
30
28
26
24
22
20
Aniline (Wt %)
0
1
2
3
4
5
6
A
B
C
D
E
F
G
H

FIG. 25

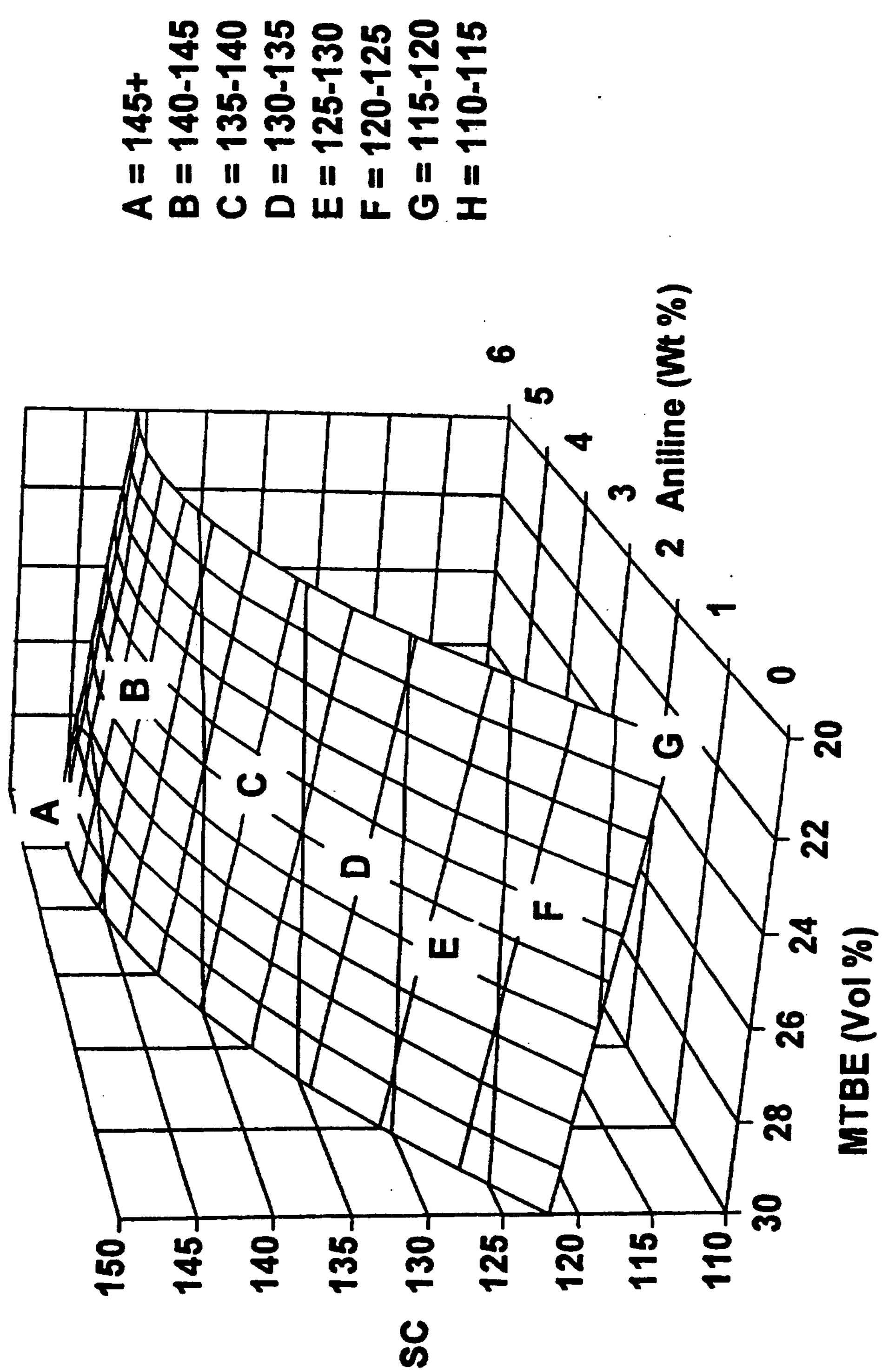

A = 145+
B = 140-145
C = 135-140
D = 130-135
E = 125-130
F = 120-125
G = 115-120
H = 110-115
A
B
C
D
E
F
G
SC
150
145
140
135
130
125
120
115
110
MTBE (Vol %)
20
22
24
26
28
30
Aniline (Wt %)
0
1
2
3
4
5
6

FIG. 26

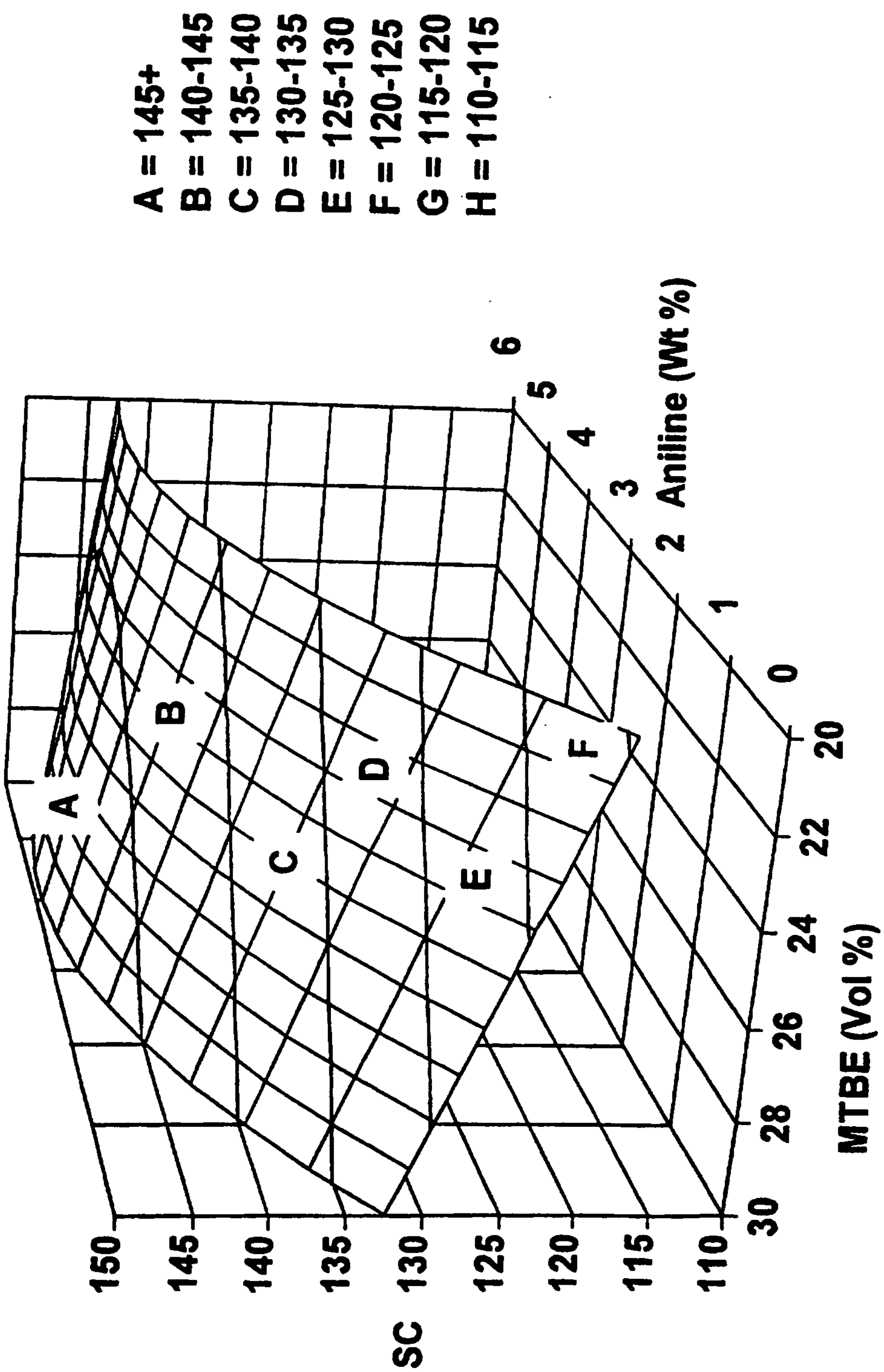

A = 145+
B = 140-145
C = 135-140
D = 130-135
E = 125-130
F = 120-125
G = 115-120
H = 110-115
SC
150
145
140
135
130
125
120
115
110
MTBE (Vol %)
30
28
26
24
22
20
Aniline (Wt %)
0
1
2
3
4
5
6
A
B
C
D
E
F

FIG. 27

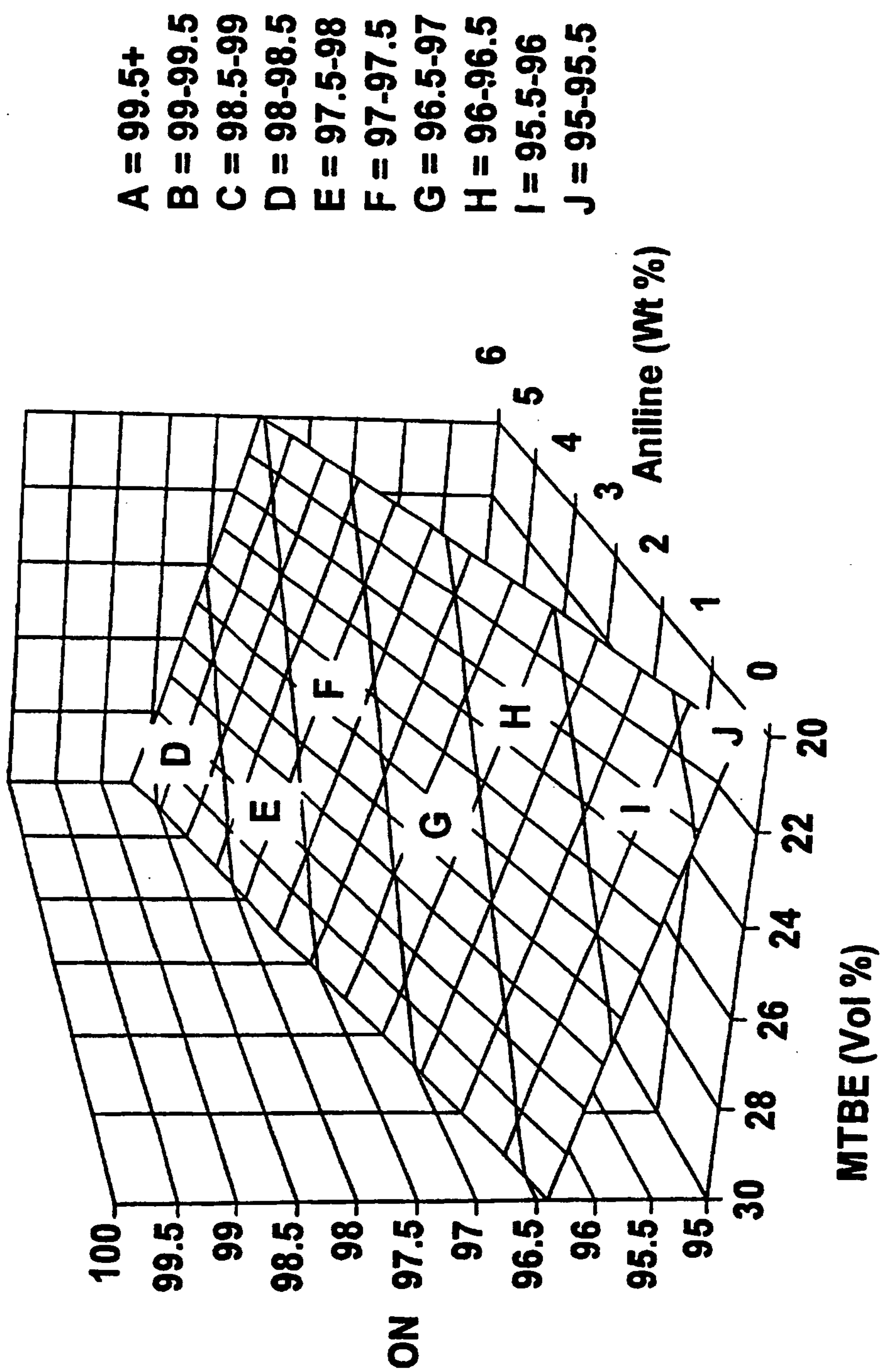

A = 99.5+
B = 99-99.5
C = 98.5-99
D = 98-98.5
E = 97.5-98
F = 97-97.5
G = 96.5-97
H = 96-96.5
I = 95.5-96
J = 95-95.5
MON
100
99.5
99
98.5
98
97.5
97
96.5
96
95.5
95
MTBE (Vol %)
30
28
26
24
22
20
Aniline (Wt %)
0
1
2
3
4
5
6
D
E
F
G
H
I
J

FIG. 28

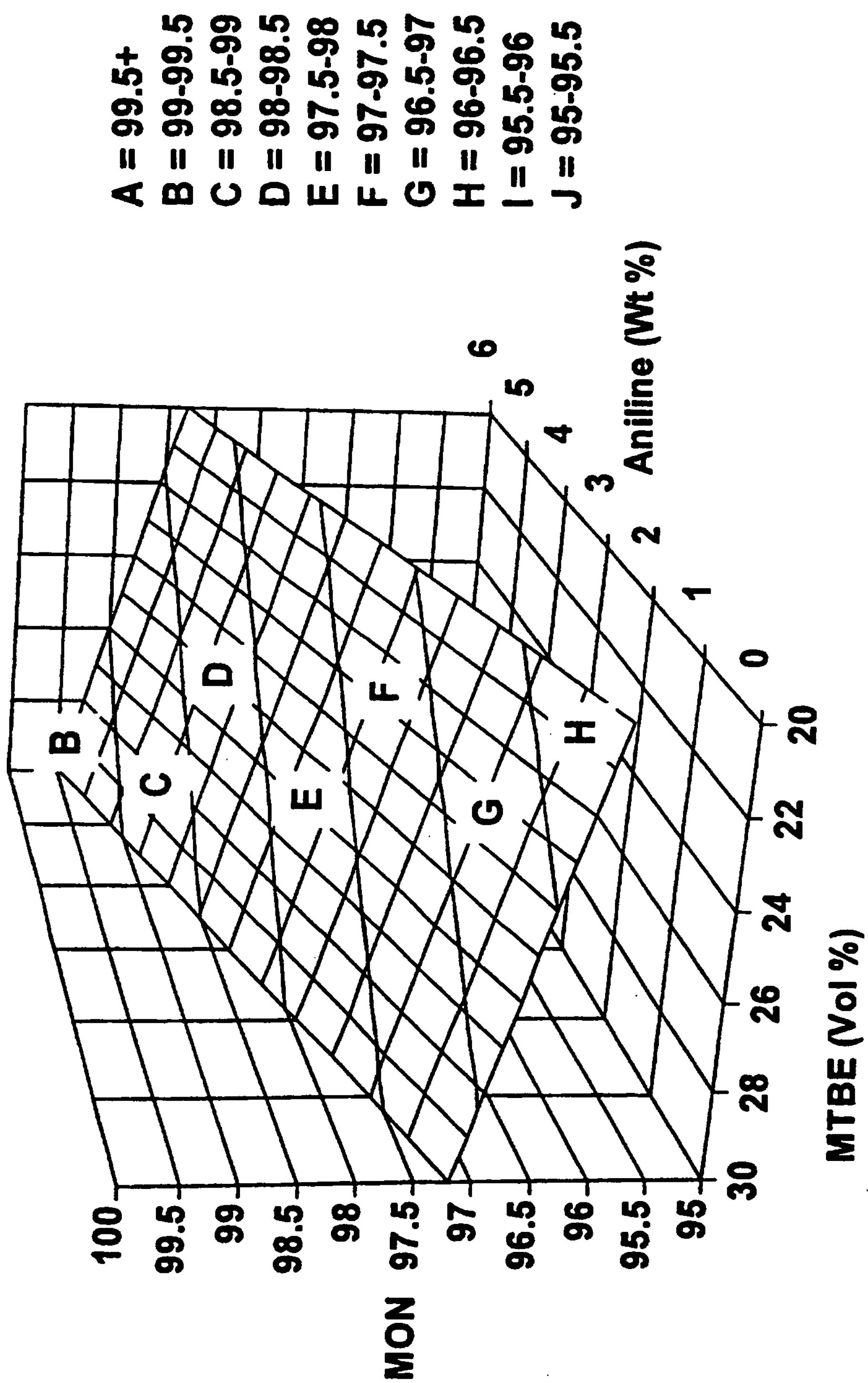

A = 99.5+
B = 99-99.5
C = 98.5-99
D = 98-98.5
E = 97.5-98
F = 97-97.5
G = 96.5-97
H = 96-96.5
I = 95.5-96
J = 95-95.5
B
C
D
E
F
G
H
Aniline (Wt %)
0
1
2
3
4
5
6
MTBE (Vol %)
20
22
24
26
28
30
MON
100
99.5
99
98.5
98
97.5
97
96.5
96
95.5
95

FIG. 29

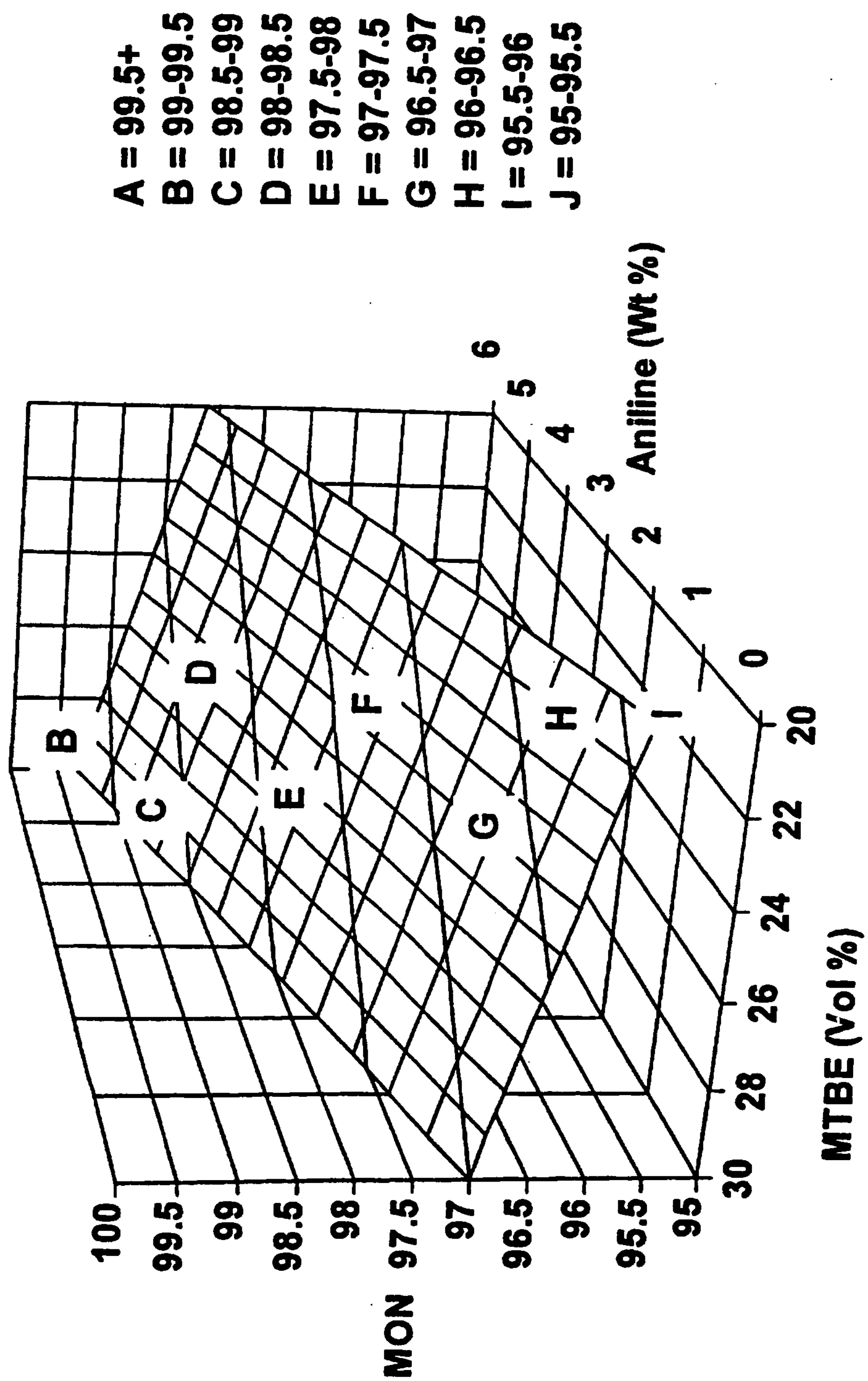

A = 99.5+
B = 99-99.5
C = 98.5-99
D = 98-98.5
E = 97.5-98
F = 97-97.5
G = 96.5-97
H = 96-96.5
I = 95.5-96
J = 95-95.5
MON
100
99.5
99
98.5
98
97.5
97
96.5
96
95.5
95
MTBE (Vol %)
20
22
24
26
28
30
Aniline (Wt %)
0
1
2
3
4
5
6
B
C
D
E
F
G
H
I

FIG. 30

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/08836

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10L1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	DATABASE WPI Section Ch, Week 9709 Derwent Publications Ltd., London, GB; Class E19, AN 97-098600 XP002039873 & RU 2 061 736 C (ACHINSK OIL REFINERY STOCK CO) , 10 June 1996	1,3,5-7, 16,18, 20-22
A	see abstract	1,10,12, 25,31

X	US 5 470 358 A (GAUGHAN ROGER G) 28 November 1995 cited in the application	1-9, 13-17, 19-24, 29-35
A	see column 2, line 10 - line 14	1,10,12, 25-27
	see column 3, line 3 - line 18 -----	

[ ] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
5 September 1997	15.09.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	De Herdt, O

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 97/08836

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5470358 A	28-11-95	EP 0697033 A	21-02-96
		WO 9425545 A	10-11-94